Co-Pyrolysis of Rice Bran Wax and Waste Plastics

Akancha

Department of Chemical Engineering
National Institute of Technology Rourkela

Co-Pyrolysis of Rice Bran Wax and Waste Plastics

Dissertation submitted in partial fulfillment

of the requirements of the degree of

M.Tech Dual Degree

in

Chemical Engineering

by

Akancha

(Roll no: 711CH1151)

based on the research carried out

under the supervision of

Prof. R.K. Singh

May, 2016

Department of Chemical Engineering

National Institute of Technology Rourkela

Department of Chemical Engineering

National Institute of Technology Rourkela

Dr. Raghubansh Kumar Singh

Professor

May 31, 2016

Supervisor's Certificate

This is to certify that the work presented in the dissertation entitled *Co-pyrolysis of Rice Bran Wax and Waste Plastics* submitted by *Akancha*, Roll Number 711CH1151, is a record of original research carried out by her under my supervision and guidance in partial fulfillment of the requirements of the degree of *M.Tech Dual Degree* in *Chemical Engineering*. Neither this dissertation nor any part of it has been submitted earlier for any degree or diploma to any institute or university in India or abroad.

Dr. Raghubansh Kumar Singh

Professor

Dedication

To my family

Akancha

Declaration of Originality

I, *Akancha*, Roll Number *711CH1151* hereby declare that this dissertation entitled *Co-pyrolysis of Rice Bran Wax and Waste Plastics* presents my original work carried out as a masters student of NIT Rourkela and, to the best of my knowledge, contains no material previously published or written by another person, nor any material presented by me for the award of any degree or diploma of NIT Rourkela or any other institution. Any contribution made to this research by others, with whom I have worked at NIT Rourkela or elsewhere, is explicitly acknowledged in the dissertation. Works of other authors cited in this dissertation have been duly acknowledged under the sections "Reference" or "Bibliography". I have also submitted my original research records to the scrutiny committee for evaluation of my dissertation.

I am fully aware that in case of any non-compliance detected in future, the Senate of NIT Rourkela may withdraw the degree awarded to me on the basis of the present dissertation.

May 31, 2016 Akancha
NIT Rourkela

ACKNOWLEDGEMENT

I consider it as my privilege to express gratitude and respect to all those who guided and inspired me in the M.Tech project. The undertaking of this project inculcated a strong sense of research inside me, and I also came to know about so many new things.

First of all, I would like to acknowledge and extend my heartfelt gratitude to Dr. R.K. Singh, Professor at Department of Chemical Engineering, National Institute of Technology, Rourkela for his exemplary guidance and constructive criticism, during the undertaking of this project entitled, "Pyrolysis of Rice Bran Wax and Waste Plastics".

I am also thankful to all the faculties and supporting staff of Department of Chemical Engineering for their constant help and extending the departmental facilities for my project.

I would like to extend my sincere thanks to my lab mates Mr. Arvind Kumar, Ms. Namrata Kumari and Ms. Debalaxmi Pradhan for their unconditional assistance and encouragement. I would also like to keep in the record the moral and emotional support provided by my parents and family throughout the period.

31 May 2016 Akancha

NIT Rourkela 711CH1151

Abstract

This work is a step towards the solution of both environmental safety and energy crisis. Tremendous use of plastic wares also leads to produce huge amount of plastics wastes. It is also pretty known that, plastics are non-biodegradable and possibly release toxic and greenhouse gases during incineration. Therefore, the investigation was the production and characterization of the oil obtained from co-pyrolysis of waste polypropylene and rice bran wax. The co-pyrolysis experiments were conducted in a semi-batch reactor within a temperature range of 400℃ to 650℃ which was obtained by Thermogravimetric analysis. The optimum pyrolytic oil at 550℃ i.e. 1:3 ratio (PP: RBW) has liquid yield of 80.5%, calorific value of 43.73 MJ/Kg. From physical characterization of oil, 800.8 kg/m^3 density, 40.75℃ flash point and 43℃ fire point, shows a very close resemblance to diesel. The chemical composition of PP, RBW and 1:3 ratio analyzed by FTIR, GC-MS and NMR spectroscopy shows that the composition of all the three oils mainly contains aliphatic compounds and small amounts of oxygenated compounds. By determining the physical and chemical characterization, it can be stated that 1:3 ratio is a mixture of diesel and gasoline. After proper treatment and refining, the pyrolytic oil can be used as a substitute of fossil fuel. The solid residue of 1:3 ratio obtained after pyrolysis was characterized for its calorific value, SEM and BET analysis. The analysis proved that the char can be utilized as activated carbon and solid fuel.

Keywords: Polypropylene; Rice bran wax; co-pyrolysis, pyrolytic oil, char

CONTENTS

Chapter No	Tiltle	Page No.

Table of Contents

List of Figures

List of Tables

Nomenclature

PP: Polypropylene

PE: Polyethylene

PS: Polystyrene

RBO: Rice Bran Oil

RBW: Rice Bran Wax

DSC: Differential Scanning Calorimetry

TGA: Thermogravimetric Analysis

GCV: Gross Calorific Value

FTIR: Fourier Transform Infrared Spectroscopy

GC-MS: Gas chromatography/Mass spectroscopy

NMR: Nuclear Magnetic Resonance Spectroscopy

SEM: Scanning Electron Microscope

BET: Brunauer Emmett Teller

Chapter1 Introduction

1.1 General Background

Plastics have molded the modern world and transformed the quality of human's life. Due to their lightweight, durability, energy efficiency, coupled with a faster rate of production and design flexibility, these plastics are employed in the entire array of industrial and domestic areas. Plastic have molded the modern world and transformed the quality of life. There is no human activity where plastics do not play a key role from clothing to shelter, from transportation to communication and from entertainment to healthcare [1].

The growth of the plastic consumption has been occurring rapidly in the last six decades due to their ability to be simply formed, its lightweight and non-corrosive behavior. These excellent properties have been used to replace the use of wood and metals. The global production of plastic has increased about 200 times from 1.5 million metric tons in the 1950s to nearly 311 million metric tons [2].

Due to excessive use of plastic results in accumulation of waste plastics which led to serious environmental problems. According to a nationwide survey, conducted in the year 2010, approximately 10,000 tones (ten thousand tons) of plastic waste were generated every day in our country (India), and only 60% of it was recycled, balanced 40% was not possible to dispose of. So gradually it goes on accumulating, thereby leading to serious disposal problems. Proper solid waste management and sanitation need to be implemented. Landfilling is not a suitable option for disposing of plastic wastes because of their slow degradation rates, require more landfill area and prevent waste compaction. The use of incinerator causes a lot of environmental controversies due to the release of toxic and greenhouse gasses [3]. It is known from the literature that heavy metals like arsenic, lead, mercury, chromium and organic chemicals such as polycyclic aromatics hydrocarbons, dioxins and furans, radioactive materials are not destroyed by incineration [4]. Polypropylene (PP) is the second largest commodity plastic material in the world, after polyvinyl chloride in terms of volume. Due to the increasing use of PP and short

life span, it is dumping in the lands, and water resources. Landfilling, incineration, and recycling methods are discarded for the proper treatment of plastic waste.

Waste plastics are one of the most favorable resources for fuel production because of its high heat of combustion, low moisture content unlike other biodegradable wastes and due to the increasing availability in local communities [5]. The conversion methods of waste plastics into fuel depend on the types of plastics to be targeted. Additionally the effective conversion requires appropriate technologies to be selected according to economic, environmental, social and technical characteristics. Polypropylene has been targeted as a potential feedstock for fuel (gasoline) producing technologies. PP thermally cracks into gasses, liquids, waxes, aromatics and char. The relative amounts of gas and liquid fraction are very much dependent on the type of polymer used. Thus, higher decomposition was observed in PP, followed by LDPE and finally HDPE.

But the main drawback of using plastic as a fuel is its high pollutant and toxic nature [6]. So there is a need for mixing plastic with other biodegradable waste, and then obtaining a next generation fuel which is non-pollutant and renewable .i.e. promoting a green environment.

As India is one of the largest producers of rice, the estimated production of rice in the year 2010-11 is about 80.44 million tons [7]. Around 18-20 % wt. % rice is rice husk which is 16 million tons annually. Due to large amount of rice husk, the residues from the processing of rice are available as energy resources. From rice husk, 16-20% of crude rice bran oil is extracted and further through winterization is converted to rice bran wax [8].

There are abundant alternative energy sources available worldwide which can be used for the replacement of fossil fuels. It is a prime importance to consider selection of the proper alternative energy considering various factors such as the availability of the source, economic value, and environmental benefit. In this respect, biomass (e.g. rice bran, coconut shells, wood-derived biomass, etc.) are the potential sources that can meet the present energy hunger. Biomass is very abundant and can be easily found in diverse forms such as agriculture residues, wood residues, energy crops and municipal solid waste [9]. Many kind of biomass have been subjected to co-pyrolysis with waste plastics to produce fuels, solvents, and other products [10]–[14]

1.2 Origin of the study

Human history for energy uses started with the utilization of sun for light and heat. From the first crude oil well discovered in 1821 [15] to the Coal Mines initiated at the same time, oil was also discovered. In the New World, the first commercial oil well was dug in 1858. But the dependency on fossil fuel and nuclear fuel will last for another 100 years. As the civilization is moving towards the era of utilizing various modern technology, the hunger for energy is increasing at an exponential rate. So it is a high time to replace the existing fossil fuel with a renewable and non-pollutant fuel like biomass, hydropower, geothermal energy, wind energy, solar energy, nuclear energy, etc to meet the energy crisis. The problem of waste management is also a big problem. The dumping of non-disposable wastes is polluting the soil, water and air.

Co-pyrolysis is a chemical process which involves two or more materials as feedstock. Many previous studies have shown that the use of co-pyrolysis can improve the characteristics of pyrolysis oil, i.e. increases the oil yield, reduce the water content present in the oil, and increase the calorific value of oil. It also helps in lowering down the oxygen content of the pyrolytic oil. This technique also contributed to avoid the use of a catalyst as it increases the operation cost and is difficult to recover after use.

Synthetic polymers like Polypropylene, Polyethylene, Polyethylene Terephthalate, Polystyrene, Polyvinyl Chloride, etc. contain higher hydrogen and carbon content than biomass and no oxygen. Therefore, plastic/biomass co-pyrolysis upgrades the bio-oil properties by increasing the carbon and hydrogen contents while reducing the oxygen present.

1.3 Research Objective

- To study the thermal co-pyrolysis of waste Polypropylene and Rice bran wax and to optimize the process experimentally for the production of liquid fuel from different ratios of PP and RBW.
- Detailed chromatographic, spectroscopic and fuel property study of the optimized liquid yield obtained from co-pyrolytic ratio for its suitability as fossil fuel substitute.
- To investigate the properties of the char samples obtained from pyrolysis.

1.4 Organization of Thesis

Chapter 1	Introduction
Chapter 2	A literature survey is done on the properties of polypropylene and rice bran wax the different recycling methods used nowadays to recover valuable products.
Chapter 3	Materials and Methods, characterization procedure for raw material, an experimental method for pyrolysis process and analysis of liquid and char product obtained in pyrolysis process.
Chapter 4	Detailed representation of results and discussions, in which explanation regarding the Thermogravimetric analysis of feedstocks, the thermal co-pyrolysis at different temperature range and the composition of the liquid product, fuel properties were studied.
Chapter 5	The conclusions based on the experiments conducted are provided, and recommendations are given for future research that can be conducted in this area.
Chapter 6	References are provided for the citations used in the thesis.

Chapter2 Literature Review

2.1 Plastics

Plastic is a material consisting of a wide range of synthetic or semi-synthetic organics that are malleable and can be molded into solid objects of diverse shapes. Plastics are typically organic polymers of high molecular mass. i.e. macromolecules, formed by polymerization and have the ability to be developed by the application of the reasonable amount of heat and pressure or some other type of force.

Polymerization is the process by which individual units of similar or different molecules combine by chemical reactions to form large macromolecules in the form of long chain structures, having altogether different properties than those of starting molecules. Several hundred and thousands of molecules combine to form the macromolecules that we call polymers [16].

Depending upon their nature and properties, the polymers are classified as Plastics, Rubbers, Elastomers, and Fibers. There are mainly two types of Plastics: Thermoplastics and Thermosetting Plastics.

Thermoplastics are those, which once shaped or formed, can be softened by the application of heat. Example: Polyethylene, Polypropylene, Nylon, Polycarbonate, etc. Applications: Polyethylene Buckets, Polystyrene Cups, Nylon ropes, etc.

Thermosetting Plastics are those, which once shaped or formed, cannot be softened by the application of heat. Example: Phenol Formaldehyde, Urea Formaldehyde, Melamine Formaldehyde, Thermosetting Polyester, etc. Applications are Bakelite Electrical switches, Formica / sermica table tops, melamine cutlery.

2.2 Waste plastics and their recycling

Waste plastics are one of the most promising resources for fuel production because of its high heat of combustion and due to the increasing availability in local communities.

Plastic wastes can be classified as industrial and municipal plastic wastes according to their origins. The conversion methods of waste plastics into fuel depend on the types of plastics used and the properties of other wastes that might be used in the process. In general, the conversion of waste plastic into fuel requires feedstocks which are nonhazardous, non-toxic and combustible. The use of catalysts also plays a major role in the quality of the products.

Table 2.1 Types of waste plastics and their recyclable products [5]

Mark	Type	Recyclable	Abbreviation	Description & Common uses
	Type 1	Yes	PET	Polyethylene Terephthalate Beverages.
	Type 2	Yes	HDPE	High-Density Polyethylene Milk, detergent & oil bottles, toys, containers used outside, parts and plastic bags.
	Type 3	Yes, But not common	PVC	Vinyl/Polyvinyl Chloride Food wrap, vegetable oil bottles, blister packages or automotive parts.
	Type 4	Yes	LDPE	Low Density Polyethylene, Many plastic bags, shrink-wraps, garment bags or containers.
	Type 5	Yes	PP	Poly Propylene. Refrigerated containers, some bags, most bottle tops, some carpets, and some food wrap.
	Type 6	Yes, but not common	PS	Polystyrenes. Through away utensils, meatpacking, protective packing.
	Type 7	Some	----------	Other. Usually layered or mixed plastic.

Waste plastic recycling is of two types

I. Mechanical reprocessing of waste plastics:

   Mechanical recycling refers to operations that aim to recover plastics waste through mechanical processes (grinding, washing, separating, drying, re-granulating and compounding).

II. Thermal or catalytic degradation of waste plastics into gas and liquid products:

   Chemical recycling via pyrolysis process is one of the promising methods to recycle waste plastics which involve thermochemical decomposition of organic

and synthetic materials at elevated temperatures in the absence of oxygen to produce fuels. The process is usually conducted at temperatures between 400-800℃. These pyrolytic products can be divided into a liquid fraction, gaseous fraction, and solid residues. Pyrolysis or thermal degradation of plastics has been investigated in many journals. There are four types of mechanisms of plastics pyrolysis i.e. end-chain scission or depolymerization, random-chain scission, chain stripping and cross-linking.

Table 2.2 classifies various plastics according to the types of fuel they can produce. It can be observed that thermoplastics consisting of carbon and hydrogen are the most important feedstock for fuel production either in solid or liquid form. From the literature study, it has been observed that PE, PP, and PS thermoplastics are desirable as feedstock in the production of liquid hydrocarbons. The addition of thermosetting plastics, wood, and paper to the feedstock leads to the formation of carbonaceous substance and lowers the rate and yield of liquid products.

Table 2.2 Classification of various plastics according to the types of fuel they produce [17]

Types of polymer	**Descriptions**	**Examples**
Polymers consisting of carbon and hydrogen	Typical feedstock for fuel production due to high heat value and clean exhaust gas.	Polyethylene, polypropylene, polystyrene. Thermoplastics melt to form solid fuel mixed with other combustible wastes and decompose to produce liquid fuel.
Polymers containing Oxygen	Lower heat value than above plastics	PET, phenolic resin, polyvinyl alcohol, polyoxymethylene
Polymers containing nitrogen or sulfur	Fuel from this type of plastic is a source of hazardous components such as NOx or SOx in flue gas.	Nitrogen:polyamide, polyurethane Sulfur: polyphenylene sulfide
Polymers containing halogens of chlorine, bromine and fluorine.	Source of hazardous and corrosive flue gas upon thermal treatment and combustion.	Polyvinyl chloride, polyvinylidene chloride, bromine-containing flame retardants and fluorocarbon polymers.

2.3 Polypropylene

Polypropylene (PP) is a crystalline thermoplastic and one of the major and versatile members of the polyolefin family. It serves dual sense of duty, both as plastic and fiber. It has an intermediary level of crystallinity between that of low-density polyethylene (LDPE) and high-density polyethylene (HDPE).aPolypropylene (PP) has the physical characteristics of stiffness, heat resistance, low specific gravity and superior workability. PP has a melting point of 171 °C (340 °F) [18], [19].

Applications

Polypropylene is used in the manufacturing of piping systems, plastic items for medical or laboratory use, food containers, beverages cups, packaging material for artistic and retail products, manufacturing carpets, rugs and mats [18], [19].

There are many research related to the thermal and catalytic pyrolysis of Polypropylene. The catalytic degradation of PP using suitable reactors (Batch, fluidized bed, fixed bed, moving bed, rotating , vacuum furnace reactor, entrained flow, wire mesh) [20] and catalysts (e.g. Silica-alumina, kaolin, ZSM etc.) and then to compare the catalytic performances by varying reaction time, temperature, catalyst to feed ratio, catalyst type with the aim to optimize the liquid yield [5], [6], [21].

Ayhan et al studied the thermal pyrolysis of waste PP, PE, and PS and determined the yields of their pyrolysis products. According to him, waste PS yielded higher liquid and waste PP and PE yielded higher gaseous products. The pyrolysis of all the three waste plastics produced a whole range of hydrocarbons comprising paraffins, olefins, naphthanes, and aromatics. PE and PP produced higher percentage of paraffins and olefins than PS [22].

2.4 Biomass

Biomass states to different organic materials that are derived from plants or animals. Biomass is non-fossilized and biodegradable organic material originating from plants,

animals, and micro-organisms. This includes the products, by-products, residues and wastes from agriculture, forestry, aquatic plants and algae municipal and industrial wastes. Biomass also includes gasses and liquids recovered from the decomposition of non-fossilized and biodegradable organic materials. It is a sustainable and renewable energy resource, constantly being formed by the interaction of CO2, air,awater, soil, and sunlight with plants and animals. It has a highest potential to contribute to the energy needs of modern society for both the developed and developing economies worldwide [23]. Biomass fuels and residues can be converted to energy sources via thermal, biological and mechanical/physical processes [24]. Biomass contains different composition of cellulose, hemi-cellulose and lignin in which cellulose is having the largest fraction.

2.4.1 Resources of biomass

The Common resources of biomass can be divided into four categories.

1. Agricultural: Agricultural production and processing wastes e.g. sugarcane bagasse, rice husk, crop residues, nutshells, and manure from cattle, poultry, and hogs.
2. Forest products: wood waste, wood or bark, sawdust, shrubs, trees, and mill scrap.
3. Municipal: sewage sludge, waste from food processing, waste paper.
4. Biological**:** animal waste, aquatic plants and algae, biological kitchen waste, human waste.

2.5 Biofuel

Biofuels are produced from living organisms or from metabolic by-products (organic or food waste products). In order to be considered a biofuel the fuel must contain over 80 percent renewable materials. Biofuels are present in the form of gas, liquid or solid fuels. It can be used as a combustible fuel for power generation, industrial applications like engines, turbines, boilers, furnaces, production of chemicals and fertilizers, adhesives, as transportation fuel which could be a good substitute for fossil fuel and as a diesel engine fuels. There is a minimum emission of greenhouse gases from the combustion of biofuel. There are primarily three routes to provide biofuels that are thermal conversion, biological

conversion and physical conversion [24]. The thermal conversion process includes pyrolysis, gasification and combustion for converting biomass to useful energy sources.

2.5.1 Combustion

Combustion is well established commercial technology with a wide application in industries. It is an exothermic reaction which involves direct burning of biomass like wood, bagasse, cow dunk cakes in boilers and furnaces which results in the production of energy in the form of heat.

2.5.2 Pyrolysis

Pyrolysis is one of the best chemical processes to convert all biomass materials into bio oil, char and volatiles. It is the most appreciated technique for chemical feedstock recycling. Pyrolysis is a technique to reduce a bulky, high polluting waste and producing energy and other valuable chemicals compounds [22]. In this process the substance is heated the absence of air or oxygen at high temperature of 400 – 1200℃. Pyrolysis of biomass generally delivers three types of products which are gaseous/volatile fractions, tar or heavy oil fractions containing volatile species, and residues. Bio-oil is produced by rapid depolymerization and then fragmenting the cellulose, hemicelluloses, and lignin components of biomass. Pyrolysis of biomass ranges from 350℃ to around 700℃. The bio-oil can be used as fuel for transportation purpose[3], [11], [20], [24]–[35].

2.5.2.1 Pyrolysis liquid composition

The liquid obtained from the pyrolysis of biomass comprises numerous organic and inorganic compounds. The general organic compounds present in the oil are Aliphatic, aromatics, amines, amides, ketones, aldehydes, phenols, alcohols, furans, acids, ethers, and other oxygenated compounds. The inorganic compounds present in the oil are mainly elements like Ca, Al, Si, Zn, Cr, Mg, Mn, Cl, Ba, Fe, K, Ni, Na, etc.

2.5.2.2 Pyrolysis gas/volatile composition

The gasses mainly consist of CH_4, CO_2, and CO. Other components present are H_2, propane, butane, etc. They can be used as a fuel for industrial combustion purpose.

2.5.3 Gasification

It is a conversion process in which feedstock is converted into gaseous fuel at high temperature by means of partial oxidation. The gas produced from gasification process is used for heat and electricity production, in engines and boilers. The gas is also used to generate fuel like methanol, and hydrogen. It is more advantageous than combustion in terms of economics, clean energy source and higher conversion efficiency [20], [22], [24], [36], [37].

2.6 Rice Bran Oil

Rice Bran Oil is natural oil extracted from the outer brown layer of rice seed. It is preferable for high-temperature cooking like stir and deep frying due to its mild flavor high smoke point of 232℃. Rice Bran contains around 15-25 % oil and can be used as a low cost raw material for fuel production [38] In many Asian countries like Japan, Indonesia, and India rice bran is used to feed cattle because of increase production. In Japan it is primarily used for cooking and termed as Heart Oil [39]. In United States and Japan, RBO is used to manufacture soaps and skin creams [40]. The physical properties of crude and refined rice bran oil are shown in the table 2.3. The composition of RBO mainly contains 37% monosaturated, 36% and 27% polysaturated fatty acid. It is edible oil mainly used for cooking and preparation of ghee.

Kasim et al [38] studied the production of biodiesel from dewaxed rice bran oil and rice bran by using supercritical methanol. Transesterification was used to produce 51.28 wt. % biodiesel. Aliphatic compounds were the major compounds present in the biodiesel. Similarly Hasan et al [40] investigated the prospects of biodiesel from rice bran in Bangladesh. He studied that the biodiesel burn up to 75% cleaner than the conventional fuels and the ozone forming emission is nearly 50% less. Transesterification is the reaction in which alcohols reacts with the fatty acids in the presence of catalyst. Density, flash point, kinematic viscosity, boiling point and calorific value obtained were very close to diesel .

Table 2.3 Physical Properties of crude & refined Rice bran oil [39]

Characters	Values(Crude rice bran oil)	Values (Refined rice bran oil)
Moisture	0.5-1.0 %	0.1-0.15 %
Density	0.913- 0.920	0.913-0.920
Refractive Index	1.4672	1.4672
Iodine Value	95-100	95-104
Saponification Value	187	187
Unsaponification Value	4.5-5.5	1.8-2.5
Free Fatty Acid	5-15%	0.15-0.2 %

2.7 Rice Bran Wax

Rice Bran is obtained inside the hull of the paddy. It is one of the major wax resources in the Asian countries because of the rice being the major cereal. The main components are aliphatic acids, and higher alcohol esters and phospholipids. The aliphatic acids mainly contains palmitic acids (C16), behenic acids (C22), lignoceric acids (C24), palmitic acids and other higher wax acids. Alcohols mainly consist of ceryl alcohol (C26), and melissyl alcohol (C30).

It is used as a substitution of carnauba wax. Other uses includes fruit and vegetable coatings, paper coatings, candles, pharmaceuticals, carbon paper, printing inks, typewriter ribbons, chewing gums, adhesives, crayons and in textile industry. In cosmetics it is used as emollient [8], [41].

Table 2.1 Chemical Properties of Rice Bran Wax [8]

Properties	Range
Melting Point (℃)	77-79
Acid Value (mg KOH/gm)	3-8
Iodine value	8-15
Saponification value(mg KOH/gm)	80-90
Color	Off-white to moderate orange/brown
Free fatty acids (%)	2.1 - 7.3

2.8 Cracking

2.8.1 Thermal Cracking

The thermal cracking involves the degradation of substances by heating in the absence of oxygen. The process is generally conducted at the temperature between 400-800℃. The reactors used for this process are fluidized bed reactors, screw kiln reactors, batch reactors etc. In this process polymers are heated at high temperatures with the breakdown of macromolecular structures into small molecules and finally producing a wide range of hydrocarbons. The various pyrolytic products are liquid, gas/volatiles and solid residues. The liquid fraction mainly consists of paraffin, olefins, naphthenes, and aromatics (PONA) [42].

2.8.2 Catalytic Cracking

The addition of catalysts improves the quality of oil. Thermal degradation of plastics has a major drawback such as very broad product range and requirement of high temperature.. The use of a catalyst is expected to reduce the reaction temperature, to promote decomposition reaction, and to improve the quality of the products [43]. The advantages of catalytic cracking are mostly in terms of the energy efficiency, with regards to the use of the reactor, the reaction temperature, and the residence time. The problems associated with the use of catalytic pyrolysis are as follows. Catalyst is consumable, has short life span due to poisoning/deactivation and, difficult to recover after use, increase in the operation cost and deposition of carbonaceous matter and impurities such as chlorine, sulfur, and nitrogen which leads to increased level of residues after pyrolysis.

2.9 Waste plastic as a liquid fuel

Due to higher content of carbon and hydrogen, plastic can be easily pyrolyzed into hydrocarbon fuels. In plastic pyrolysis long macromolecular structures are broken down into smaller molecules or oligomers. Further degradation of molecules depends on reaction time, temperature, catalyst type and other conditions [44]. The liquid yield from the plastic pyrolysis has a quite close calorific value as compared to other conventional fuels, which are in between 40-45 Mj/Kg. Ayhan et al studied that the total yield of

paraffin and olefins produced from polypropylene and polyethylene waste pyrolysis are higher than that of polystyrene [22].

Table 2.2 Comparison of Regular Gasoline with Plastic waste fuel [45]

Properties	**Regular gasoline**	**Plastic waste fuel**
Color	Orange	Pale yellow
Specific gravity at 28 °C	0.7423	0.7254
Specific gravity at15 °C	0.7528	0.7365
Gross calorific value	11210	11262
Net calorific value	10460	10498
API gravity	56.46	60.65
Sulphur content(by mass)	0.1	<0.002
Flash point (Abel) °C	23	22
Pour point °C	<-20	<-20
Cloud point	<-20	<-20

2.10 Advantages of Co-pyrolysis

It is a process which involves two or more material as feedstock. Many studies have investigated the use of co-pyrolysis to improve the physical and chemical characteristics of the pyrolytic oil such as increase in the liquid yield, low oxygen content, high calorific value, low water content, low production cost and waste management at the same time [11]. The co-pyrolysis method is more consistent to produce homogenous pyrolytic oil than the blending oil method. In co-pyrolysis reaction, the interaction of radicles encourages more stabilized oil and minimum phase separation [13]. Other parameters include the biomass/plastic ratio and the type of reactor used.

2.11 Co-pyrolysis of biomass with waste plastics

Huiyan surname et al [46] described catalytic co-pyrolysis of pine sawdust and different waste plastics such as PP, PE, PS in a fuidized bed reactor taking the effect of temperature, plastic/biomass ratio, different plastics and catalysts into consideration. This work was primarily done to increse the yields of aromatics and olefins.

Pradhan et al [47] investigated the production of bio-oils from the co-pyrolysis of mahua seeds and polystyrene. The results showed that at a temperature of 525℃, and a blend ratio of 1:1 the yield was optimum i.e. 71%. After further physical and chemical characterization of the bio-oil it was concluded that the synergetic effect incresed the yield and quality of the bio-oil.

Abnisa et al [48] investigated the co-pyrolysis of waste polystyrene and palm shell to obtain liquid fuel taking temperature, reaction time and feed ratio as parameters. The maximum oil of 68.3 wt. % was obtained at 600℃ for the blend ratio of 60:40, and a reaction time of 45 minutes. The oil showed a very high calorific value of 40.34 Mj/Kg a, water content as 1.9 wt. % and oxygen content of 4.24 wt.%. The oil mainly contained aliphatic and aromatic hydrocarbons.

Marin et al [49] reported the thermal co-pyrolysis of wood biomass and synthetic polymers in a rotating autoclave. From the TGA report it was observed that the biomass degraded at a lower temperature than the olefins. The co-pyrolysis resulted in utilzation of lignocellulosic and plastic wastes to produce bio-oils at an optimum teperature of 400℃.

Martinez et al [13] studied the co-pyrolysis of biomass with waste tyres in a fixed bed and in an augter reactor. The radical interaction between waste tyres and biomass pyrolysis products promote the formation of a stable bio-oils with upgraded properties.

Chapter3 Experimental

3.1 Materials

3.1.1 Waste Polypropylene:

Waste Polypropylene (used plastic disposable glasses) was collected from the Lecture Annexure, National Institute of Technology Rourkela campus waste disposal courtyard and used in the experiment. The waste plastic disposable glasses were cut into small pieces by a pair of scissor (approx. $1cm^2$) and the flakes were directly used in the experiment (Figure 3.1).

Figure 3.1 Disposable polypropylene glass, and shredded glass

3.1.2 Rice Bran Wax (RBW):

Rice Bran Wax was collected from a rice mill in Raipur, Chhattisgarh. The rice bran wax was mashed and the mashed wax was used in the pyrolysis experiment.

Figure 3.2 Mashed Rice Bran Wax

3.2 Methods

3.2.1 Differential Scanning Calorimetry (DSC) Analysis:

Differential Scanning Calorimetry is a method to study the thermal transitions of a polymer, i.e. what happens to a polymer when it is heated to a range of temperature. DSC is beneficial to conduct the measurements for melting points, heats of reaction, glass transition temperature, heat capacity and oxidative stabilities [50]. The waste plastic glasses and rice bran wax were identified by determining melting temperature from DSC curve of the samples (Figure 3.3, 3.4). From the figure 3.3, the melting point of plastic glasses was found out to be 166 ℃ which ensures the sample to be polypropylene [5], similarly from the figure 3.4, the melting point for RBW is 79℃ which ensures the sample to be Rice Bran Wax [8].

The thermal analysis was carried out in a NETZSCH DSC 200F3 instrument in an aluminum crucible. 5 mg of PP was taken in the closed aluminum crucible with temperature ranging from 24℃ to 200 ℃, keeping the flowrate of nitrogen gas as 60 ml/min, for time duration of 40 minutes.

Similarly, 21 mg of RBW was taken in a closed aluminum crucible with temperature ranging from 27℃ to 150 ℃, keeping the flowrate of nitrogen gas as 60 ml/min, for a time duration of 30 minutes.

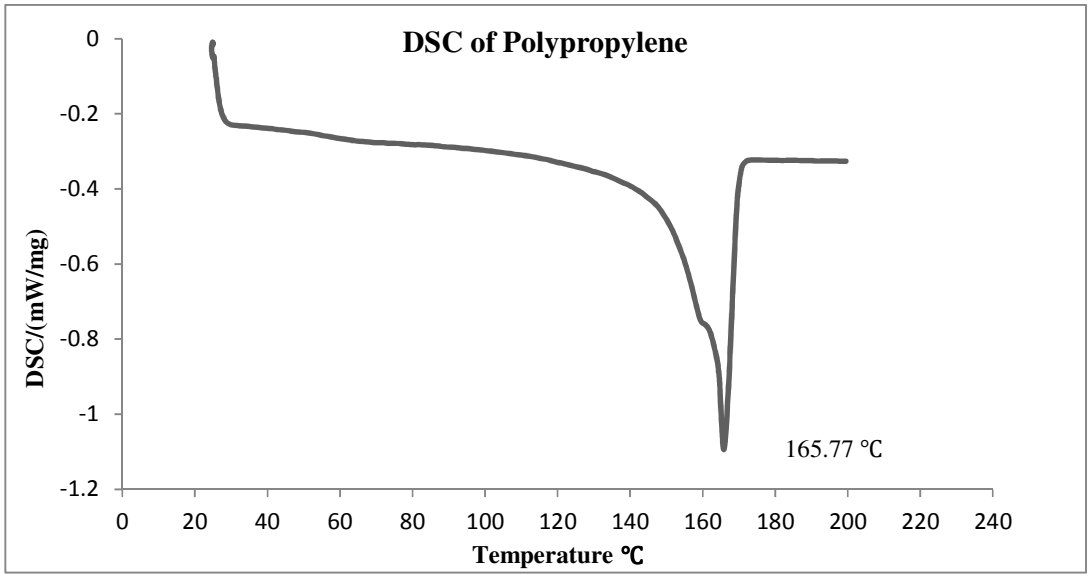

Figure 3.3 DSC of Polypropylene

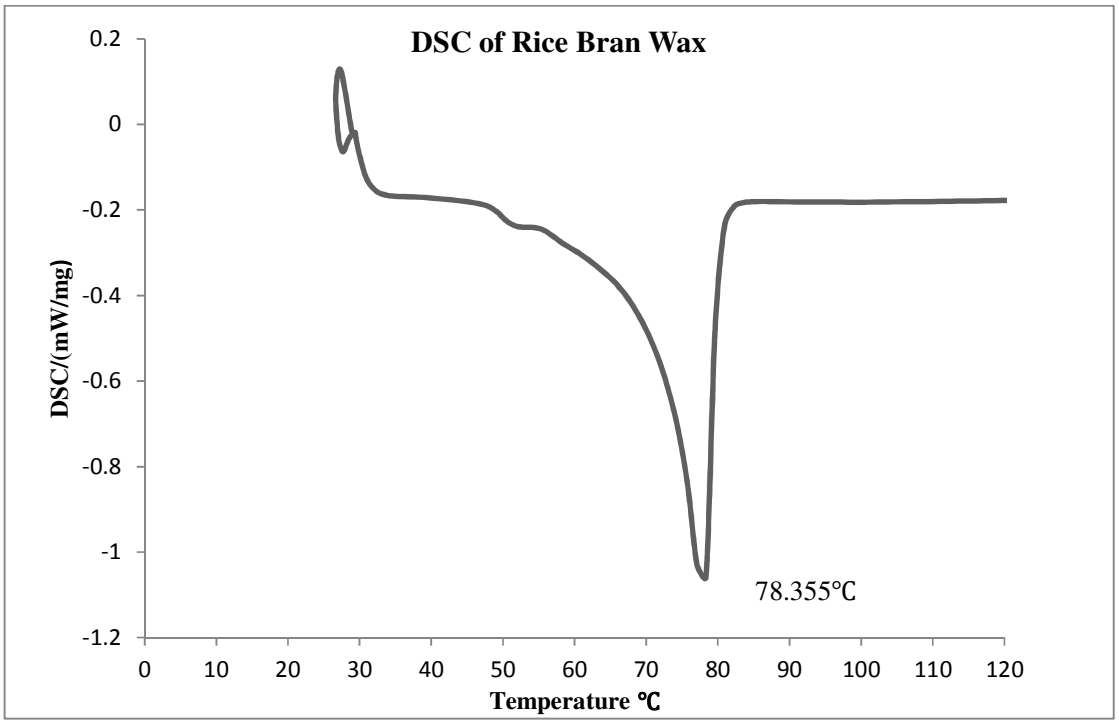

Figure 3.4 DSC of Rice Bran Wax

3.2.2 Thermogravimetric Analysis

The TGA analysis of Polypropylene, Rice Bran Wax and 1:1 ratio raw material was carried out in a DTG-60 Series, TOSHVIN (Serial No: C30564300281TK)thermal

analyzer. A known weight of the sample was heated in a platinum crucible at a constant heating rate of 10 °C/min operating in a stream of N2 atmosphere with a flow rate of 50ml/min from 25 °C to 800 °C. The TGA graph was shown in figure 4.1 to 4.3

3.2.3 Proximate & Ultimate Analysis of Feedstocks:

The proximate analysis which includes the determination of moisture, volatile matter, ash, and fixed carbon is primarily carried out to ascertain the quality of the raw materials. The procedure was followed according to ASTM D3173-75. Volatile matter constitutes those compounds which are driven off as volatiles by heating while fixed carbon refers to the remaining constituents after the release of volatiles excluding ash and moisture content [4]. The Ultimate analysis was carried out using a VARIOEL CHNS (serial number: 11064047) elemental analyzer. It is also known as elemental analysis which determines the carbon, hydrogen, nitrogen, sulfur and the oxygen content in the material. The oxygen component of the material is calculated by difference after the calculation of carbon, hydrogen, nitrogen and sulfur content. The calorific value of the plastic was obtained by using a bomb calorimeter (Model: Parr 6100 Digital Bomb Calorimeter). The waste plastic (0.3860 gm) was placed inside the bomb calorimeter and burned in the presence of oxygen keeping initial temperature 35.57℃ and jacket temperature as 36.85 ℃. The temperature rise in the whole process is around 1.8151℃ to determine the gross heat. Similarly for rice bran wax, the sample (0.4966 gm) was placed inside the bomb calorimeter and burned in the presence of oxygen keeping initial temperature 35.91℃ and jacket temperature as 36.68 ℃. The temperature rise in the whole process is around 2.0428℃ to determine the gross heat. Similarly for rice bran wax (0.4966 gm) was taken in a crucible. The temperature rise was 2.0428 ℃. The I.S. 1448: P: 6 protocol was followed in determining the GCV. Table 3.1 shows the proximate and ultimate analysis of Polypropylene and Rice Bran Wax.

Table 3.1 Proximate & Ultimate analysis of Polypropylene & Rice Bran Wax

Types of Used Raw Materials	Polypropylene	Rice Bran Wax
Proximate Analysis		
Moisture content	0.67	5.45
Volatile matter	98.64	90.41
Ash content	0.24	1.54
Fixed carbon (By difference)	0.45	2.6
Ultimate Analysis		
Carbon (C)	82.15	76.26
Hydrogen (H)	13.27	15.13
Nitrogen (N)	0.01	0.02
Sulphur (S)	2.84	1.68
Oxygen (O)	1.74	6.91
Empirical Formula	$C_1H_{1.94}N_{0.0001}S_{0.013}O_{0.016}$	$C_1H_{2.38}N_{0.0001}S_{0.007}O_{0.06}$
C/H Molar ratio	0.52	0.42
C/O Molar ratio	62.27	14.80
Gross Calorific Value (MJ/Kg)	46.44	40.65

3.2.4 Pyrolysis experimental set up:

The pyrolysis setup used in this experiment is a batch reactor shown in Figure 3.5 and 3.6. It consists of a reactor made of stainless steel tube (length- 145 mm, internal diameter- 37 mm and outer diameter- 41 mm) sealed at one end and an outlet tube at another end for obtaining the volatile/gas/oil products of the reaction. The stainless steel tube is heated externally by an electric furnace, with the temperature being measured by a Cr-Al: K type thermocouple fixed inside the reactor and temperature is controlled by external PID controller. The PID controller was used to monitor the temperature of the furnace. The accuracy of this PID controller is ± 0.3% FS (FS = 1200ºC). So the temperature can be measured with ±3.6ºC.

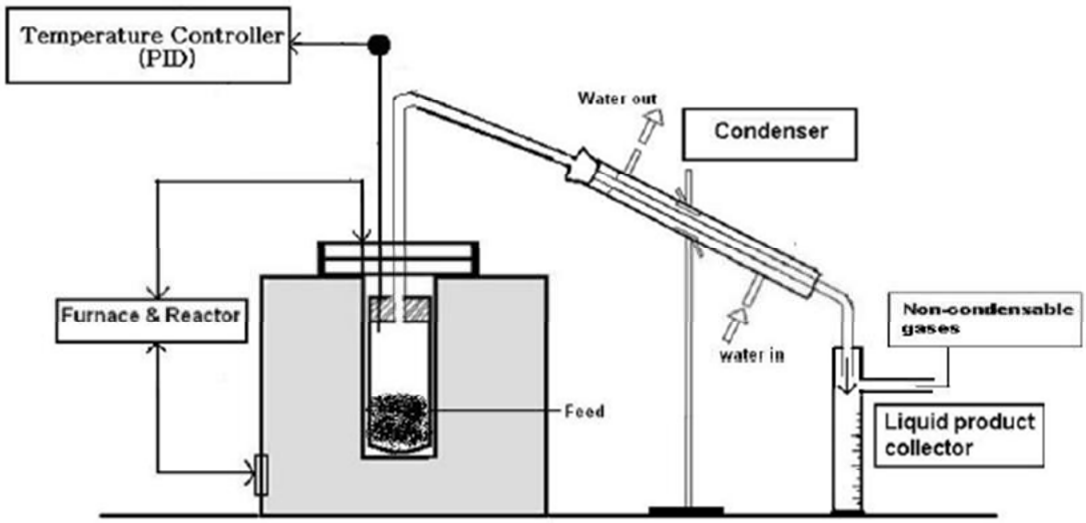

Figure 3.5 Schematic representation of pyrolysis experimental setup

Figure 3.6 Pyrolysis experimental setup

Figure 3.7 Stainless steel reactor

3.2.5 Sample Pyrolysis Run:

Sample Pyrolysis Run is done to find out the optimum temperature at which liquid product i.e. the oil yield attains maximum yield. The temperature range was taken based on the TGA results. A total of 20 grams of the feedstock (taking different ratios of Rice Bran Wax and Polypropylene) is taken for thermal pyrolysis at the intervals of 25℃ starting from 300℃ to 650℃. The analytical balance of CONTECH INSTRUMENTS LTD, NAVI MUMBAI, and Model: CAS-243 was used to measure the weight of the samples. This machine capacity is 230 gram and accuracy are 0.0001 gram. During these runs, various parameters were recorded such as reaction time, liquid yield, residue and yield of gas/vapor that escape into the air. The variation of these parameters was plotted against time. The other attributes such as texture, viscosity, color, and odor were also observed.

3.2.6 Characterization of pyrolysis oil:

The pyrolytic oil has been characterized for physical and chemical properties.

3.2.6.1 Physical properties of pyrolytic oil:

Physical properties such as Kinematic viscosity, conradson carbon residue, flash point, fire point, pour point, calorific value of the pyrolytic oil was determined using the following Indian Standard methods, which is shown in Table 3.2.

Table 3.2 Test Methods

Test Methods	Properties
Specific Gravity	I.S.1448 P.16
Density	I.S.1448 P.16
Kinematic Viscosity	I.S.1448 P.25
Conradson Carbon Residue	I.S:1448 P:122
Flash Point	I.S.1448: P:20
Fire point	I.S:1448 P:20
Pour Point	I.S.1448 P:10
Gross Calorific Value	I.S. 1448: P:6

The density and specific gravity measurement were done with an accuracy of ±0.0005gm/cc and the other parameters such as pour point, flash point and fire point was measured with ±1ºC accuracy.

3.2.6.2 Chemical properties of pyrolytic oil:

3.2.6.3 Fourier transformation infrared spectroscopy (FTIR):

The oil was analyzed using Fourier Transform Infrared spectroscopy (FT-IR).The FTIR spectra were collected in the range of 400-4000 cm-1 region with 8cm-1 resolution. The FTIR imaging is carried out using Perkin Elmer RX.

3.2.6.4 Gas chromatography and mass spectroscopy (GC/MS):

The GC-MS analysis of the oil sample was carried out to know the exact composition of the oil. The composition of oil derived from co-pyrolysis of rice bran wax and polypropylene was analyzed using Gas Chromatography/Mass spectrometry (7890B GC System/5977A MSD Agilent Technologies). All the compounds were identified using the NIST library. The GC-MS analysis was done on the basis of the programming which is given below.

GC CONDITION: 7890B GC System

Oven Column Temperature: 70˚C

Temperature of Injection: 250˚C

Mode of Injection: Split

Split Ratio: 10

Flow Control Mode: Linear Velocity

Column Flow: 1.51 ml/min

Carrier Gas used: Helium 99.9995% purity

Volume of injection: 1 microliter

Column Oven Temperature Program

Rate	Temperature (˚C)	Hold Time (min)
-	70.0	3.0
10	300	9.0 [34.0 mts total]

COLUMN: 5977A MSD

Length: 30.0m

Diameter: 0.25mm

Thickness of film: 0.25um

MS CONDITION

MS LIBRARY

Temperature of Ion source: 230 °C

NIST Library

Temperature of Interface: 240°C

Scan range: 40 – 700 m/z

Solvent cut time: 5mins

MS start time: 5(min)

MS end time : 35 (min)

Ionization: EI (-70ev)

Scan speed: 2000

3.2.6.5 Nuclear magnetic resonance spectroscopy (NMR):

The ^{1}H NMR spectra were recorded by using a 400 MHz/54 mm Ultra Shield, Ultra hold time, BRUKER DPX-400, High-performance digital FT-NMR spectrometer where chloro- form-d containing TMS (tetramethylsilane) used as the internal standard.

3.2.7 Characterization of pyrolytic char:

3.2.7.1 Proximate and ultimate analysis of the char

The proximate analysis of char samples was dome according to the ASTM D3173-75 method. The elemental analysis was conducted using VARIOEL CHNS (serial number: 11064047) elemental analyzer. The calorific value was obtained using a bomb calorimeter (Model: Parr 6100 Digital Bomb Calorimeter) by following the I.S. 1448: P: 6 protocol.

3.2.7.2 SEM Analysis:

The char product obtained from the PP: RBW ratio pyrolysis was characterized by Scanning Electron Microscope (Model: NOVA NANO SEM450_CR_NITRKL) at different magnification values to observe a clear view on porosity and diameter. The physical morphology of the char was studied by SEM

3.2.7.3 BET Analysis:

The surface area of char was estimated by nitrogen absorption at 77.35K using an automatic adsorption instrument (Quantachrome® ASiQwin™-/Instrument name-: Autosorb iQ Station 1). Before finding the gas adsorption measurement, the char was outgassed in the vacuum chamber at 250℃ for a time of 5 hours to remove the moisture and other impurities that were sticked to the surface of the char sample.

Chapter4 Results and Discussion

4.1 Thermogravimetric Analysis:

Thermogravimetric analysis is a thermal analysis technique in which decomposition of material is measured with respect to change in temperature and time keeping the heating rate constant. In the present work TGA was carried out for Polypropylene, Rice Bran Wax and 1:1 ratio for determining the thermal stability/decomposition in various ranges of temperature.

4.1.1 Decomposition of Polypropylene, RBW and 1:1 ratio

Figure 4.1, 4.2, and 4.3 represents the variations of weight loss (TGA curve) with respect to reaction temperature. The samples (2.5-4 mg) were taken in a platinum crucible at a heating rate of 10°C/min in a nitrogen atmosphere for a temperature range of 24°C to 800°C for all the three samples. For all the feedstock taken, two decomposition stages was observed.

For Polypropylene, the degradation started at 24℃ and the 50% weight loss occurred at 375℃. The thermograph showed that first decomposition started from 24℃ to 300℃. It was due to the slow vaporization of moisture. The second stage of decomposition occurred in between 300℃ to 400℃ [21]. The sharp decline in the curve results in maximum weight loss of around 90 % due to the decomposition of the volatile matter. The complete decomposition of PP occurred at 410 ℃ after that no residue was observed [22], [51]–[53]. The residue signifies the presence of ash content in the material.

From the thermograph of Rice Rran Wax, the decomposition started from 30℃ and the 50% mass loss occurred at 386℃. The first degradation started from 30℃ to 370℃ due to the vaporization of moisture present in the RBW. The decomposition is

more rapid as compared to PP due to the presence of moisture or water content in the wax [47]. The second stage of occurred in between 370°C to 410°C. It is due to the presence of volatile matter. The content of volatiles is less than PP. After 410°C, there was a small amount of residue left in the crucible which was finally decomposed at around 540°C. The slow decomposition of residue is due to the presence of cellulose, hemicellulose, and lignin [47]. This shows high ash content compared to PP.

Similarly, 50 wt. % each of PP and RBW was taken in a platinum crucible and TGA curve was plotted. For 1:1 ratio the decomposition started from 31°C and continued till 800°C, at a constant heating rate of 10°C/min. The first decomposition was observed from 31°C to 350°C and then second degradation occurred from 350 °C to 475°C. The sudden decline in the curve revealed a good percentage of volatile matter. After 450°C no residue was observed. The degradation curve of 1:1 was in between that of PP and RBW. Therefore from the TGA analysis it could be stated that blending of PP and RBW can be used as a raw material to produce bio-oil because of the presence of less moisture and ash content and high volatile matter. According to the TGA results pyrolysis temperature range was decided and further product distribution was obtained experimentally.

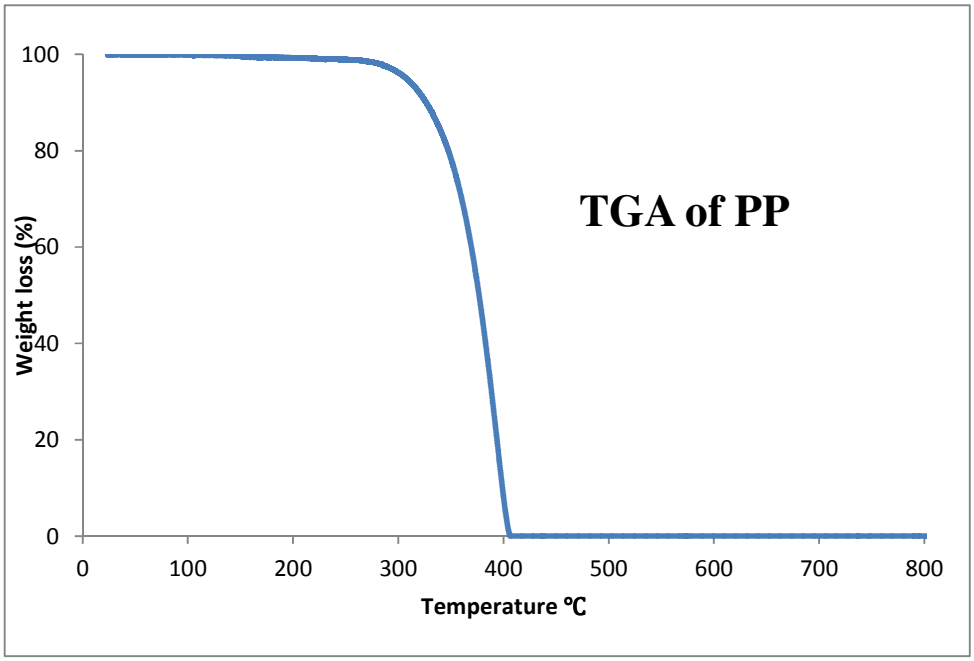

Figure 4.1 TGA of Polypropylene

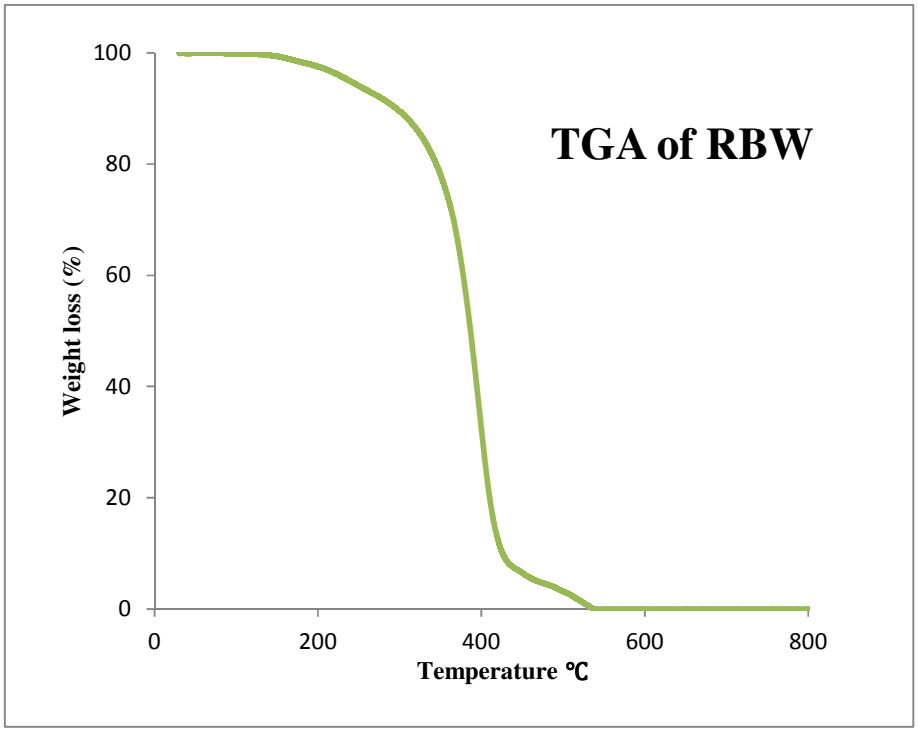

Figure 4.2 TGA of RBW

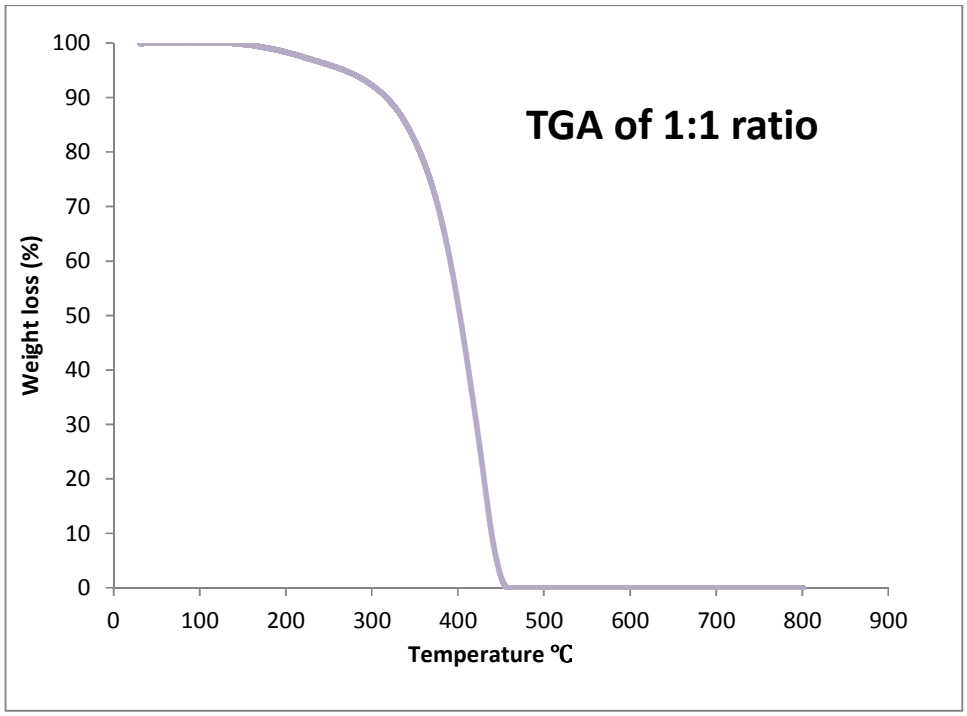

Figure 4.3 TGA of 1:1 ratio

4.2 Proximate and ultimate analysis of PP and RBW

From the table 3.1, it was inferred that the volatile matter of PP and RBW is 98.64% and 86.41. The presence of volatiles favours the production of large amount of pyrolytic oil. High volatile comtent provides high volatility and reactivity, which are quite favourable for production of liquid fuel. The low ash content for both the raw materails favours high liquid yield. The ultimate analysis of PP and RBW shows a higher content of carbon with a very low percentage of oxygen. The low percentage of oxygen depicts low corrosion, more stability and high calorific value. The low sulfur content proves that it is safe to use it as a feedstock to produce next generation fuel.

4.3 Effect of temperature on product distribution

The pyrolysis of Polypropylene, Rice Bran Wax, and different ratios of PP and RBW (i.e. 1:1, 1:2, 1:3, 2:1, 3:1) yielded three different products i.e. liquid, gas, solid residue or char. The distributions of these fractions are different at different temperatures and are shown in Figure 4.4 to 4.11 and in Table 4.1 to 4.7.

For polypropylene, the condensable fractions (oil) obtained at low temperature i.e. in between 400℃ to 500℃ were less viscous, whereas that obtained above 450℃ were highly viscous. The oil yield was quite low at 400℃ (42.70 wt. %), but with an increase in temperature the liquid yield reached 75.59 wt. % at 500℃ and then gradually decreased with further increase in temperature. The optimum oil was obtained at a reaction time of 30 minutes. The vapor/volatile fractions increased at low temperatures leading to low liquid yield. At low temperature, the reaction time was high due to strong secondary cracking of the pyrolysis product occur inside the batch reactor.
Similarly, the low liquid and high gaseous yield at higher temperature was due to the formation of more non-condensable gaseous/volatile fractions by severe cracking. The oil was cracked at higher temperature so that the product will be rich in olefins. The presence of olefins causes instability and form deposits that damages the equipment by blocking pumps, pipelines and tips of the burners [22].

For Rice Bran Wax, the temperature range was taken in between 400℃ to 650℃. The optimum oil obtained was 86.5 wt. % at 600℃. With increase in temperature there is an

increase in viscosity of oil. It is due to severe cracking inside the reactor. Similar to PP, the percentage of residue decrease with increase in temperature but the reaction time decreased with the rise in temperature. The optimum oil was obtained at a reaction time of 30 minutes.

For all the other blends the product distribution trends were pretty similar to that of PP and RBW. As the constituent of RBW was increasing (e.g. 1:0, 1:1, 1:2, 1:3), the liquid was getting highly viscous. This is due to better cracking of RBW as compared to PP.

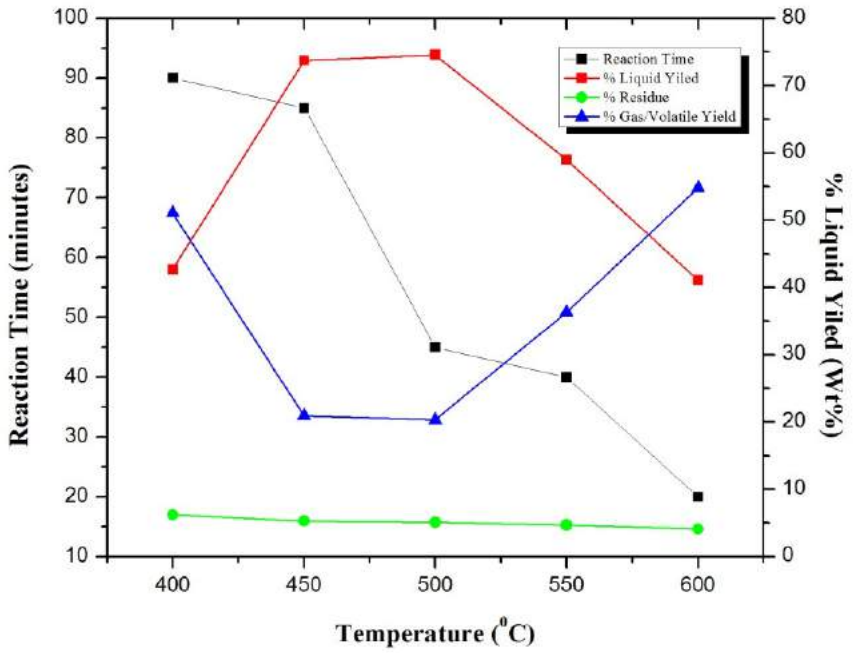

Figure 4.4 Product distribution of Polypropylene

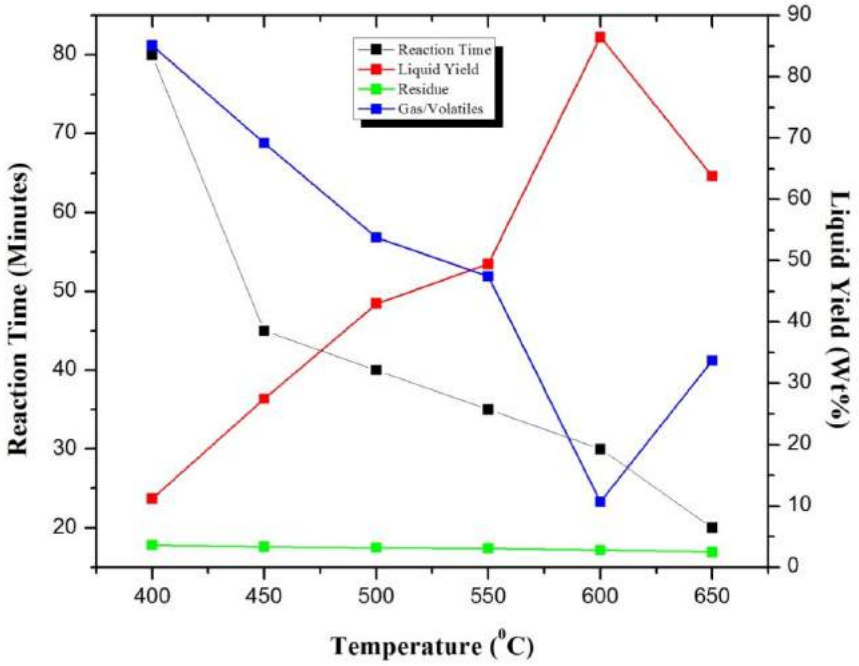

Figure 4.5 Product distribution of RBW

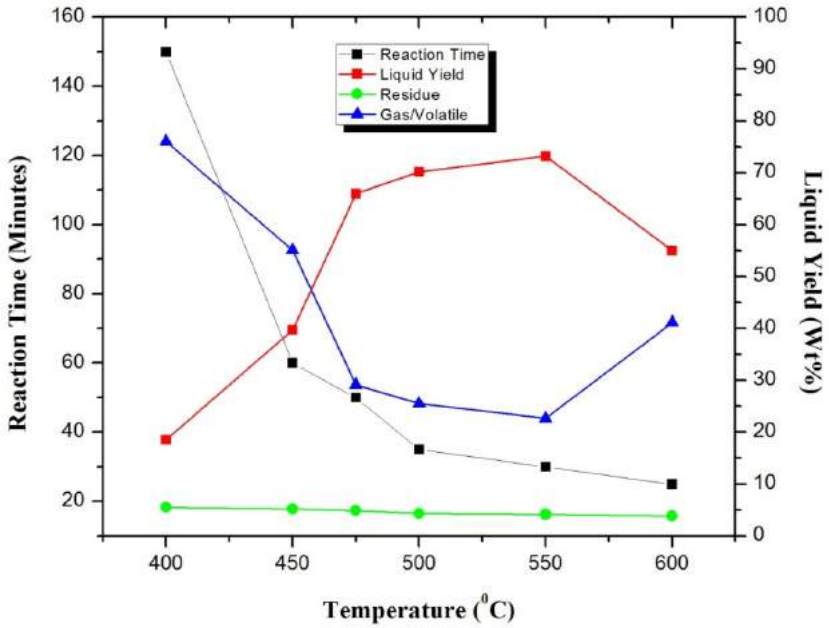

Figure 4.6 Product distribution of 1:1 (PP: RBW)

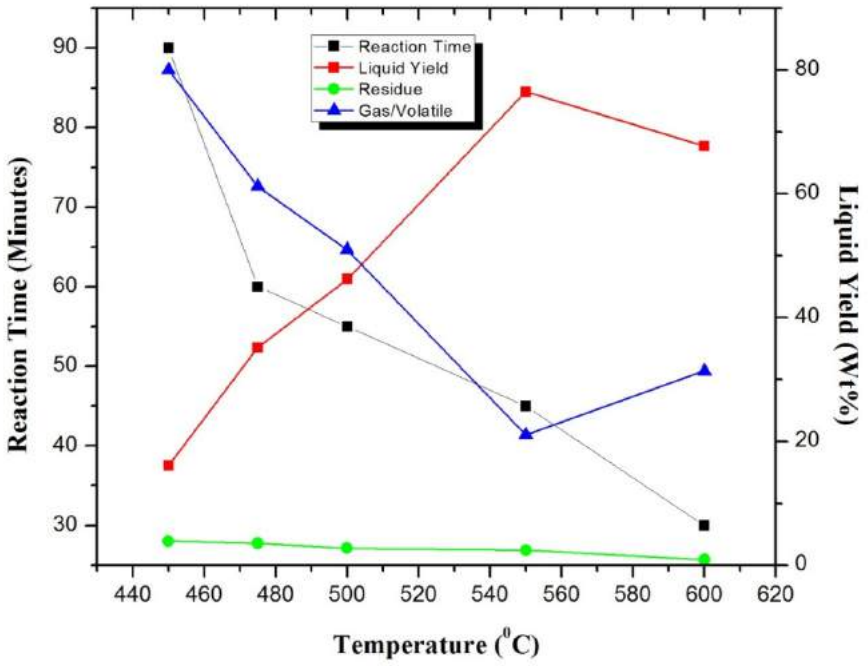

Figure 4.7 Product distribution of 1:2 (PP: RBW)

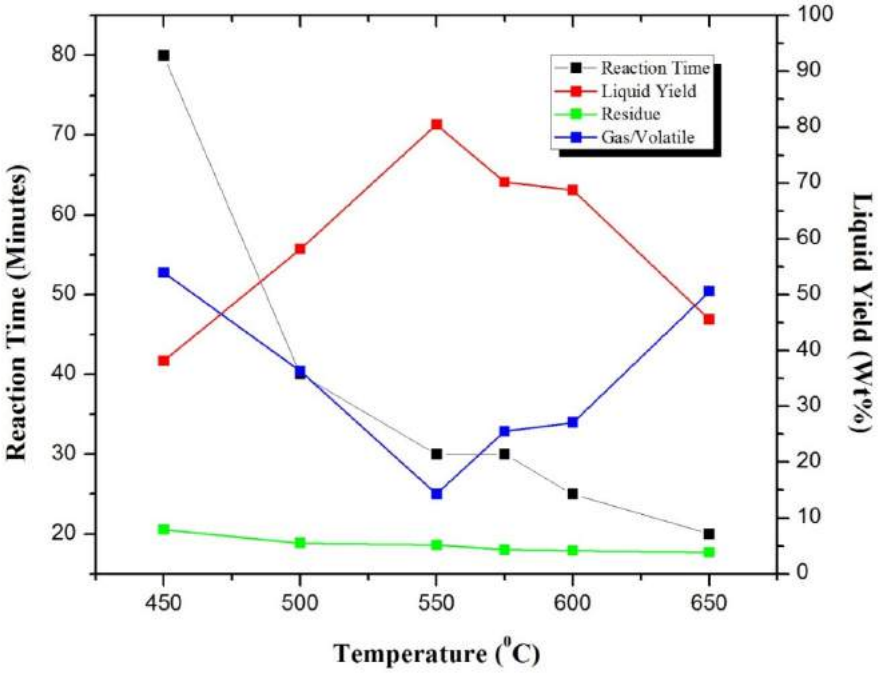

Figure 4.8 Product distribution of 1:3 (PP: RBW)

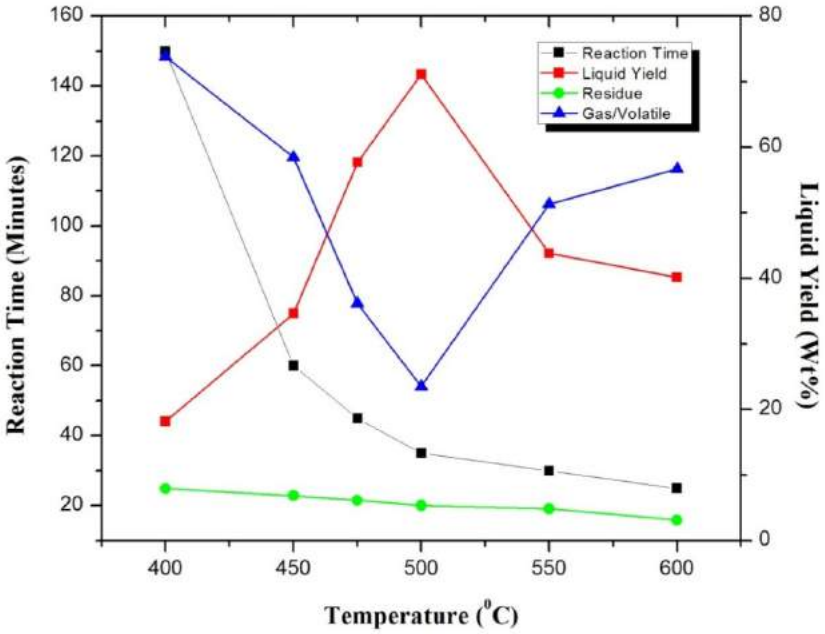

Figure 4.9 Product distribution of 2:1 (PP: RBW)

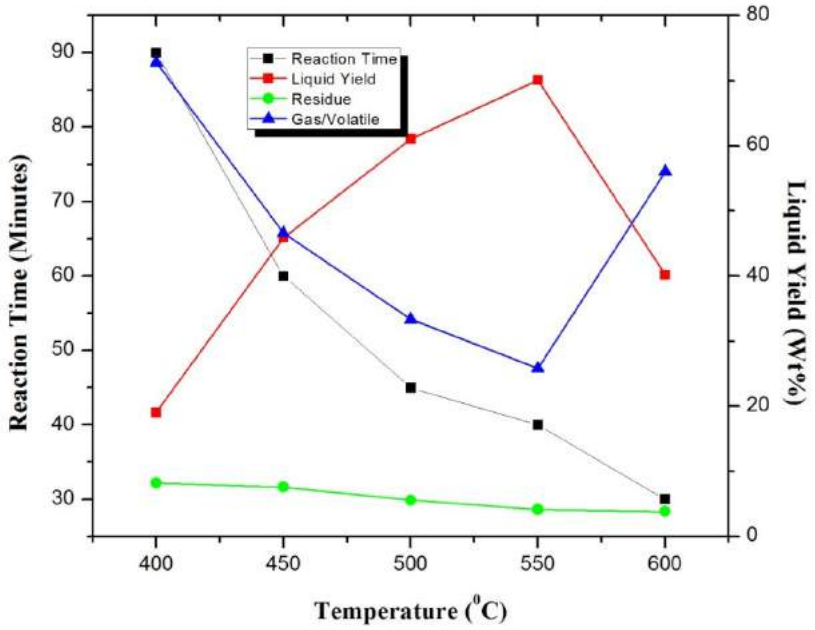

Figure 4.10 Product distribution of 3:1 (PP: RBW)

Table 4.1 Product distribution of Polypropylene pyrolysis

Temperature(℃)	Liquid Yield (wt. %)	Gas Yield (wt. %)	Residue Yield (wt. %)	Reaction Time (min)
400	42.70	51.10	6.20	90
450	73.74	20.96	5.30	85
500	75.59	20.31	5.10	45
550	59.00	36.30	4.70	40
600	41.10	54.81	4.10	20

Table 4.2 Product distribution of Rice Bran Wax pyrolysis

Temperature(℃)	Liquid Yield (wt. %)	Gas Yield (wt. %)	Residue Yield (wt. %)	Reaction Time (min)
400	11.22	85.10	3.67	80
450	27.47	69.22	3.33	45
500	43.00	53.80	3.20	40
550	49.43	47.47	3.10	35
600	86.5	10.70	2.80	30
650	63.79	33.37	2.50	20

Table 4.3 Product distribution of 1:1 pyrolysis

Temperature(℃)	Liquid Yield (wt. %)	Gas Yield (wt. %)	Residue Yield (wt. %)	Reaction Time (min)
400	18.48	76.02	5.5	150
450	39.73	55.07	5.2	60
475	65.95	29.15	4.9	50
500	70.18	25.52	4.3	35
550	73.18	22.65	4.17	30
600	55.01	41.16	3.83	25

Table 4.4 Product distribution of 1:2 pyrolysis

Temperature(℃)	Liquid Yield (wt. %)	Gas Yield (wt. %)	Residue Yield (wt. %)	Reaction Time (min)
450	16.08	80.03	3.89	90
475	35.17	61.27	3.56	60
500	46.23	50.99	2.78	55
550	76.5	21.07	2.43	45
600	67.73	31.38	0.89	30

Table 4.5 Product distribution of 1:3 pyrolysis

Temperature(℃)	Liquid Yield (wt. %)	Gas Yield (wt. %)	Residue Yield (wt. %)	Reaction Time (min)
450	38.14	53.96	7.9	80
500	58.14	36.36	5.5	40
550	80.5	14.30	5.2	30
575	70.18	25.52	4.3	30
600	68.74	27.09	4.17	25
650	45.55	50.52	3.83	20

Table 4.6 Product distribution of 2:1 pyrolysis

Temperature(℃)	Liquid Yield (wt. %)	Gas Yield (wt. %)	Residue Yield (wt. %)	Reaction Time (min)
400	18.18	73.87	7.95	150
450	34.64	58.51	6.85	60
475	57.68	36.19	6.13	45
500	71.15	23.51	5.34	35
550	43.81	51.34	4.85	30
600	40.18	56.7	3.12	25

Table 4.7 Product distribution of 3:1 pyrolysis

Temperature(℃)	Liquid Yield (wt. %)	Gas Yield (wt. %)	Residue Yield (wt. %)	Reaction Time (min)
400	19	72.8	8.20	90
450	45.85	46.59	7.56	60
500	61.07	33.36	5.57	45
550	70.07	25.81	4.12	40
600	40.15	56.04	3.81	30

4.4 Selection of the best pyrolytic oil

In the table 4.8, the best pyrolytic oil is selected for further physical and chemical characterization. The standard error was calculated by repeating every experiment thrice and results were considered by one-way analysis of variance (ANOVA). For calorific value, the interpretation of standard error is taken from the literature and therefore the error was taken as ± 1 MJ/Kg.

By analyzing the above table, we notice that as the amount of PP is increasing, the liquid yield is getting low, and as the amount of RBW is increasing, the yield of liquid is increasing, which is maximum for 1:3 ratio. Another important point to consider is the calorific values. The calorific value of 3:1 is the highest among all the pyrolytic oils, which is 44.76 MJ/Kg which is more as compared to that of gasoline and diesel [53]. Hence 1:3 ratio is chosen for further physical characterization in accordance with IS 1448 methods.

Table 4.8 Optimum Results

Sample	Optimum Temperature(℃)	Liquid Yield (wt. %) $\pm$ standard error	Reaction Time(min)	Calorific Value (MJ/Kg)
PP (1:0)	500	74.5 $\pm$ 5.6	85	41.63
RBW (0:1)	600	86.5 $\pm$ 2.7	30	40.18
1:1	550	73.18$\pm$ 1.4	30	38.12
2:1	550	71.5 $\pm$1.8	35	40.22
3:1	550	70.07 $\pm$ 2.1	40	39.44
1:2	550	76.5 $\pm$ 2.4	45	41.3
1:3	**550**	**80.5 $\pm$ 3.1**	**30**	**43.76**

Now the low-density liquid was separated from the pyrolytic liquid by centrifuging the pyrolytic oils for around 10 minutes with 1000-3000 g. The figure 4.11 shows the separation of high-density liquid (oils) and low-density liquid.

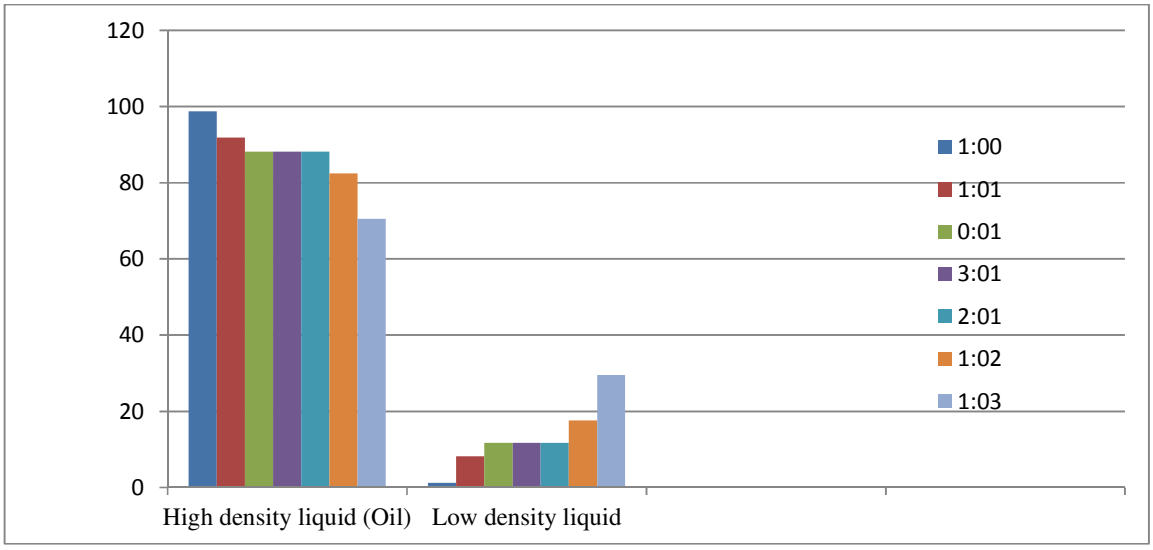

Figure 4.11 Separation of High Density Liquid (Oil) and Low-density liquid

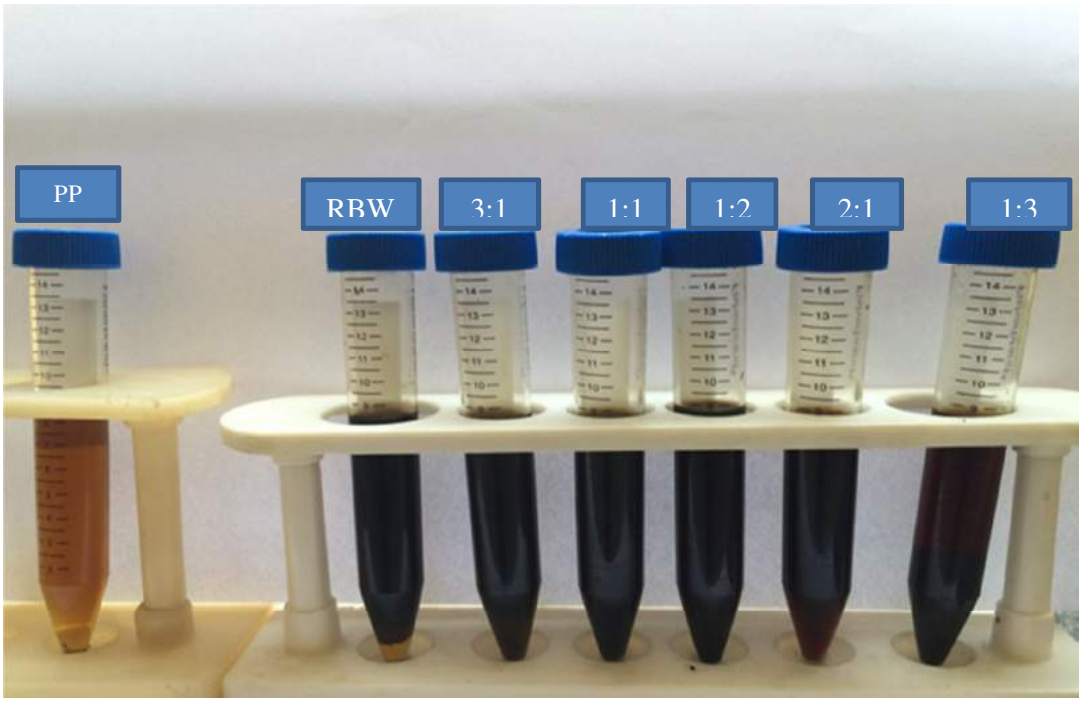

Figure 4.12 Separation of High density liquid and Low density liquid

4.5 Characterization of pyrolytic oil

4.5.1 Physical characterization of pyrolytic oil

The optimum oil obtained after thermal pyrolysis of 1:3 ratio appears dark brown in color with strong acidic smell resembling petroleum fractions. The oils were characterized regarding both fuel properties and chemical composition. The fuel properties of the pyrolytic oil were analyzed by IS-1448 method and compared with diesel and gasoline that has been summarized in Table 4.9.The table illustrates that the density of the 1:3 pyrolytic oil was same as that of diesel and gasoline. The kinematic viscosity of the oil was lower than that of diesel. The low viscosity is convenient in the handling and transportation of the oil. Conradson Carbon residue was found to be greater than that of diesel and gasoline. Carbon residue of a fuel is the tendency to form carbon deposits under high temperature conditions in an inert atmosphere. The flash point of the oil was around 41 ℃, which is in the comparable range. It is generally the minimum temperature at which the oil sample produces sufficient vapors which when mixed with air forms an inflammable mixture which ignites momentarily. If the flame continued to burn for a minimum of 5 seconds, it is termed as fire point. The pour point is quite high, i.e. it solidifies at 20 ℃. The gross calorific value of the oil was in-between diesel and gasoline. It is the amount of energy produced by complete combustion of a fuel.

Table 4.9 Physical properties of 1:3 pyrolytic oil

Properties	**1:3 Oil**	**Gasoline**	**Diesel**
Density (Kg/m3)	800.8	700 to 800	820 to 860
Specific Gravity	0.8008	0.70 to 0.80	0.82 to 0.86
Kinematic Viscosity @100℃ (centistokes)	0.76	NA	2 to 4.5
Kinematic Viscosity @50℃ (centistokes)	5.032	N/A	N/A
Conradson Carbon Residue (%)	1.03	N/A	0.30
Flash Point ℃	40.75	23	40 to 50
Fire Point ℃	43	20 to 25	40 to 50
Pour Point℃	22.7	<-20	<-20
Gross Calorific Value (MJ/Kg) (High Heating Value HHV)	43.76	45.7	43 to 47

4.5.2 Chemical characterization of pyrolytic oils

4.5.2.1 CHNS analysis of Pyrolytic oils

Table 4.2 showed the elemental composition of all the pyrolytic oils (i.e. Oils obtained from 1:0, 0:1, 1:1, 1:2, 1:3, 2:1, 3:1) and compared with diesel. From the analysis, it can be observed that the carbon percentage of all the pyrolytic oils is less than that of diesel oil. The oxygen content was calculated by mass balance equation. It was moreover same as that of diesel. Due to the low oxygen content, the gross calorific value of all the oils is close to diesel. The low oxygen content of all the oils results in less corrosion problems.

Table 4.10 CHNS analysis of Pyrolytic oils

Element	PP oil	RBW oil	1:1 oil	1:2 oil	1:3 oil	2:1 oil	3:1 oil	Diesel
C	80.43	76.56	81.61	82.38	83.47	82.34	83.36	85.72
H	17.56	15.78	17.33	16.64	16.14	16.55	15.82	13.2
N	0.01	0.02	0.04	0.03	0.01	0.04	0.01	0.18
S	1.43	0.84	0.778	0.56	0.32	0.42	0.36	0.3
O	0.57	6.80	0.242	0.39	0.055	0.65	0.45	0.6
GCV(MJ/Kg)	41.63	40.18	38.12	41.3	43.76	40.22	39.44	43 to 47
C/H	0.38	0.404	0.39	0.413	0.43	0.414	0.439	0.541
C/O	186.11	14.8	453.33	286.25	2047.05	167.31	248.21	190.4

4.5.2.2 FTIR analysis of pyrolytic oils

Fourier Transform Infrared spectroscopy (FTIR) is an important chemical analysis technique which identifies various characteristic functional groups present in oil. On interaction of an infrared ray with oil, chemical bond will contract, stretch and absorb infrared radiation in a specific wave length range regardless the structure of the rest of the molecules. The monoatomic elements like Helium, Neon, Argon, Krypton (generally all noble gasses) and homopolar diatomic molecules like H_2 N_2, O_2 do not absorb infrared

light. On the basis of this fundamental principle functional group present in the pyrolytic oils were detected. The FTIR spectrum for all the three pyrolytic oils (PP oil, RBW oil and 1:3 oil) is shown in Figure 4.12 and results found from the transmittance spectrums are presented in Table 4.11, Table 4.12,and Table 4.13. The data of polypropylene showed the presence of mainly aliphatic compounds, with the small contribution of alkyl halides and alcohols. From the table of rice bran wax, it might be concluded that the RBW pyrolytic oil mainly contain aliphatic compounds with the small composition of ethers. The best pyrolytic oil i.e. 1:3 oil, which could be analyzed on the basis of maximum yield and highest calorific value showed the presence of aliphatic compounds. There were some amounts of aromatics, alkyl halides, amines and ketones.

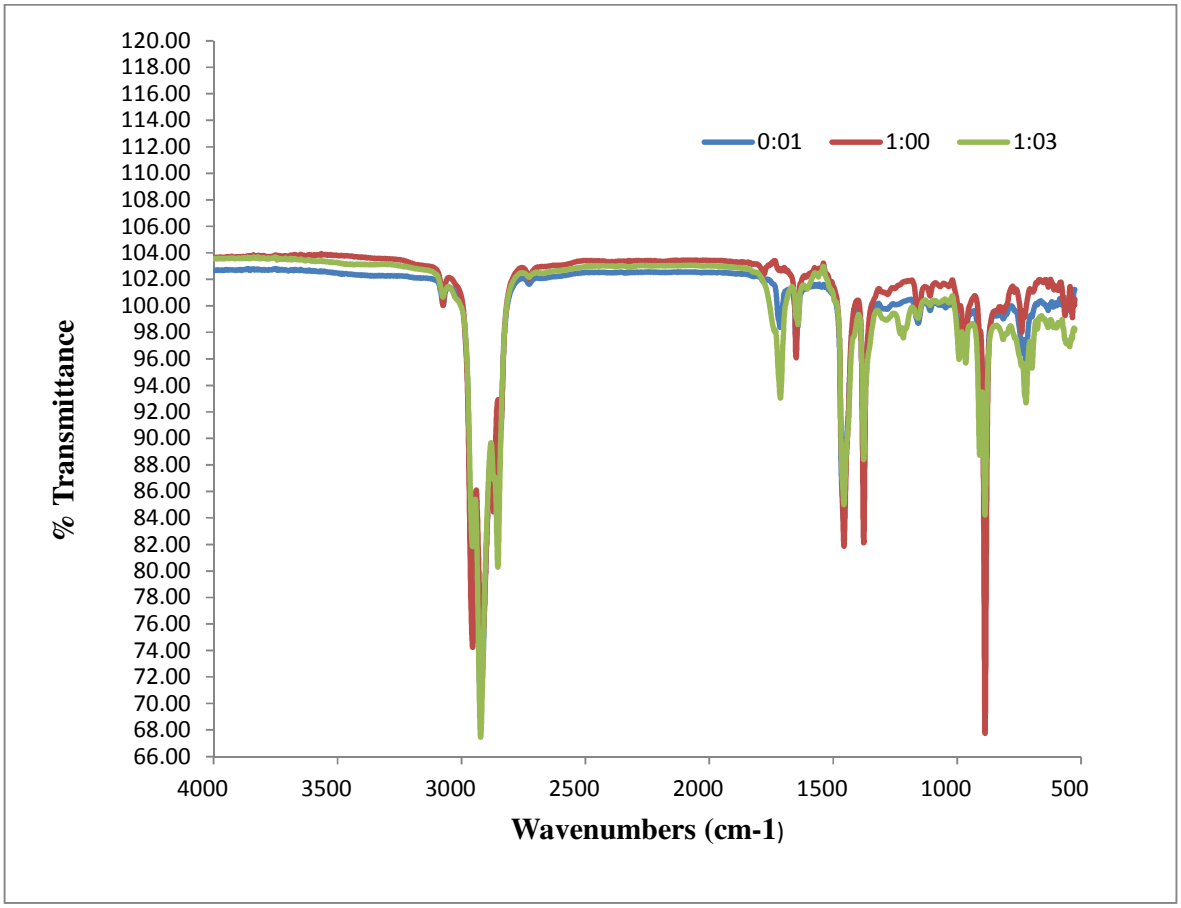

Figure 4.13 FTIR Spectra of PP, RBW, and 1:3 pyrolytic oils

Table 4.11 FTIR functional groups of polypropylene oil

Absorption Ranges(cm^{-1})	**Functional Group**	**Types of Vibrations**
534, 564	Alkyl halides(R-Br)	C-Br stretch
739	Aromatics	C-H Bend
886	Alkenes	=C-H bend
965	Alkenes	=C-H bend
1155	Alcohols	C-O stretch
1376	Alkanes and Alkyls	CH3 C-H bend
1456	Alkanes	C-H bend
1649	Alkenes	C=C stretch
2842	Alkanes	C-H stretch
2870	Alkanes	C-H stretch
2913	Alkanes	C-H stretch
3074	Alkenes	=C-H stretch

Table 4.12 FTIR functional groups of Rice Bran Wax

Absorption Ranges(cm^{-1})	**Functional Group**	**Types of Vibrations**
721	Alkyls	-(CH2)n Bending
887	Alkene	=C-H bend
909	Alkene	=C-H bend
965	Alkene	=C-H bend
1377	Ethers	C-O Stretching
1456	Alkanes	H-C-H Bending
2853	Alkanes	H-C-H Asymmetric & Symmetric Stretching
2870	Alkanes	H-C-H Asymmetric & Symmetric Stretching

Table 4.13 FTIR functional groups of 1:3 pyrolytic oil

Absorption Ranges(cm^{-1})	**Functional Group**	**Types of Vibrations**
546	Alkyl halides(R-Br)	Strong C-Br stretch
698	Aromatics	Strong, C-H bend
722	Alkenes	Medium, broad =C-H bend
887	Alkenes	Strong =C-H bend
909	Alkenes	Medium+Strong =C-H bend
965	Alkenes	Strong =C-H bend
991	Alkenes	Medium+Strong =C-H bend
1217	Alcohols	Medium-strong C-O stretch
1377	Alkanes	Medium CH(CH3)2 or -(CH3)3 bend
1456	Aromatics	Medium-strong ring C=C stretch
1642	Amines	Weak-medium N-H bend

1713	Ketones	Strong, C=O stretch
2853	Alkanes	Strong C-H stretch

4.5.2.3 GC-MS Analysis of pyrolytic oils

GC-MS is one of the modern analytical techniques to identify the probable compound present in the pyrolytic oil derived from the waste plastic and biomass. Analysis using gas chromatography/mass spectrometry confirmed the composition of each fraction. GC-MS analyses were investigated for the PP, RBW, and 1:3 pyrolytic oils which were obtained at a temperature of 500°C, 600℃ and 550℃ respectively. The NIST software was used to examine the peaks provided by the chromatogram which is shown in Table-4.14, 4.15 and 4.16. From all the tables given below it was observed that more than 70 compounds were identified to be present in the pyrolytic oil samples by GC-MS analysis as shown in the GC-MS figure 4.13,4.14 and 4.15. Taking into consideration of the percentage area, the highest peak areas of the total ion chromatogram of the compounds were mainly aliphatic compounds (29%). The compounds present in PP oil are mostly the aliphatic hydrocarbons (alkanes and alkenes) with carbon number ranging from C_4-C_{15}. The constituent of amines and amides are around 16.5%. In addition, some oxygenated compounds such as alcohol, ketone, aldehydes, etc. are also found in the oil. For RBW oil, the major composition was of aliphatic, amines and amides (55%). The carbon number ranges from C_5 to C_{15}. Large numbers of oxygenated compounds were also present in the oil where aldehydes (12.36%) and ketones (36.15%) were the major contributors. In 1:3 pyrolytic oil, the trend was pretty similar to that of PP and RBW oils. The major constituents were of aliphatic and amines which contribute to around 60.76%. The carbon number range from C_3 to C_{20}.There is a good share of ketones which is around 46%. Acids and ethers contribute to around 27%.

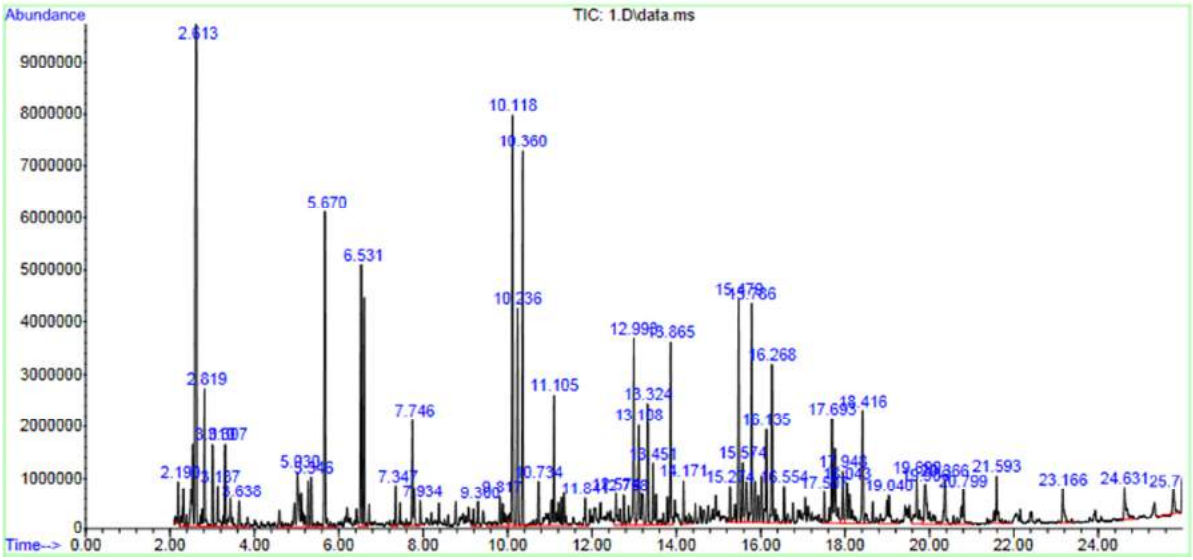

Figure 4.14 GC-MS of polypropylene oil at 500 °C

Table 4.14 GC-MS analysis of polypropylene pyrolytic oil

Compound Name	**Area %**
Aliphatic and Aromatics	28.03
Amines and Amides	16.53
Ketones	23.26
Aldehydes	5.61
Alcohols & Phenols	10.78
Acids and esters	3.94
Other heterocyclic acids	4.56

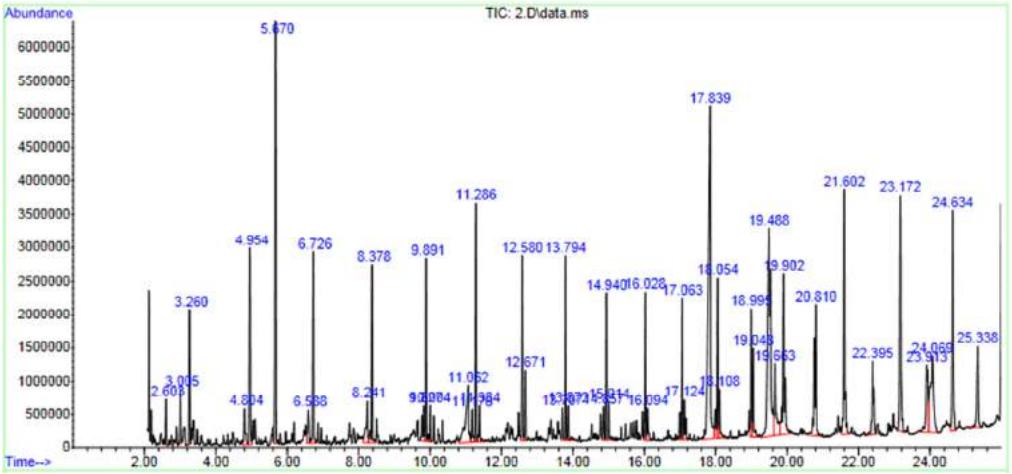

Figure 4.15 GC-MS of Rice Bran Wax oil at 600 °C

Table 4.15 GC-MS analysis of rice bran wax pyrolytic oil

Compound Name	Area %
Aliphatic and Aromatics	24.45
Amines and Amides	30.15
Ketones	36.15
Aldehydes	12.36
Alcohols & Phenols	26.12
Acids and esters	5.07
Other heterocyclic acids	8.06

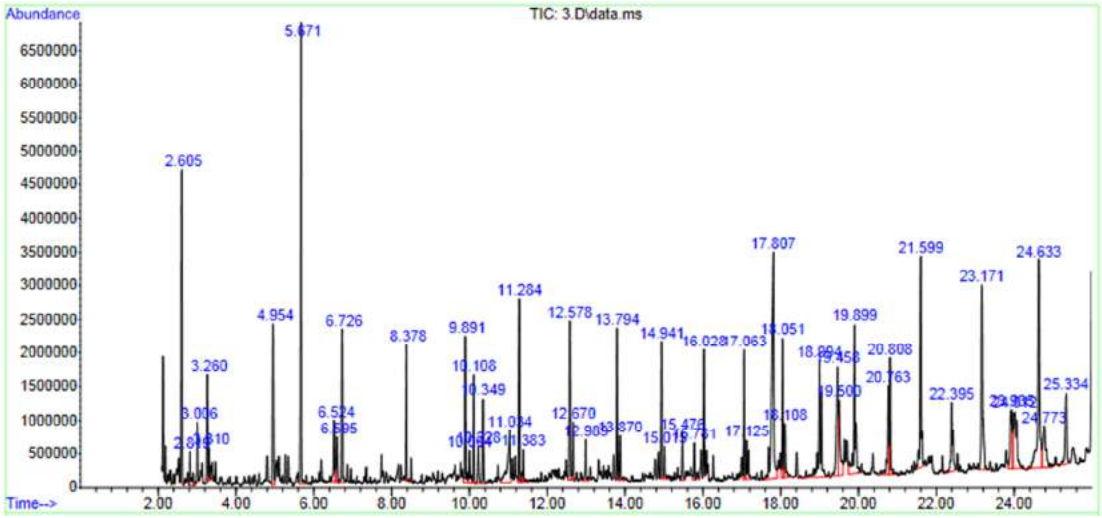

Figure 4.16 GC-MS of 1:3 pyrolytic oil at 550℃

Table 4.16 GC-MS analysis of 1:3 ratio pyrolytic oil

Compound Name	Area %
Aliphatic and Aromatics	25.72
Amines and Amides	37.20
Ketones	46.37
Aldehydes	9.77
Alcohols & Phenols	5.77
Acids and esters	27
Other heterocyclic acids	12.47

4.5.2.4 NMR of Pyrolytic oils

1H NMR is performed to estimate the hydrocarbon types and to provide an indication of product quality. The percentage of alkanes is around 60.72, which is the major share in the whole NMR spectra. The alkanes and aromatics are around 90%. The higher percentage of

alkanes, naphthenes, and aromatics are highly desirable for production of gasoline [22]. The total percentage of hydrogen present in olefins is around 10%.

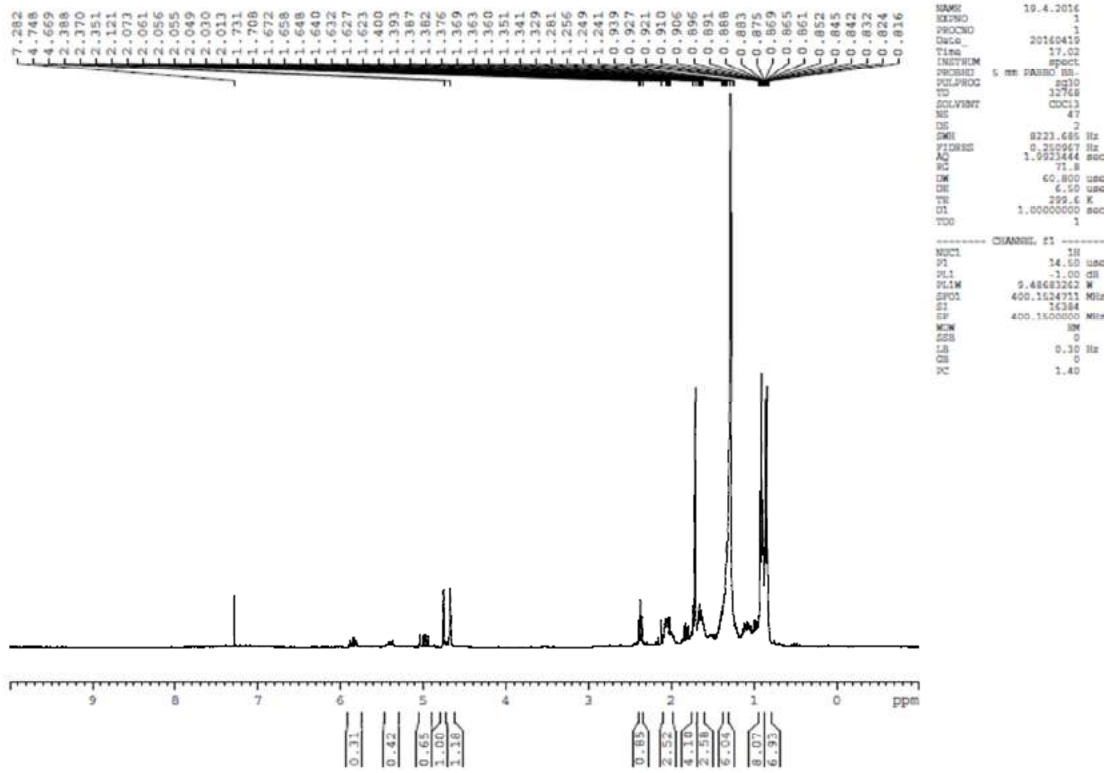

Figure 4.17 **The** ^{1}H NMR spectra of polypropylene pyrolytic oil

Table 4.17 NMR analysis of polypropylene pyrolytic oil

Hydrogen type	**Chemical shift (ppm)**	**Total hydrogen (%)**
Alkane C-H	0.8-1.5	60.72
Allylic, benzylic, adjacent to sp^2 carbon	1.5-2.4	29.01
Alkene =CH	4.6-5.1	8.17
Alkene =CH	5.3-5.9	2.12

From the NMR spectra of RBW oil, it was observed that the major constituent was of alkanes having a total percentage of hydrogen as 58.42 %. The presence of olefins was very less, i.e. around 9%. The lower percentage of olefins is needed for stabilized and less corrosive oils.

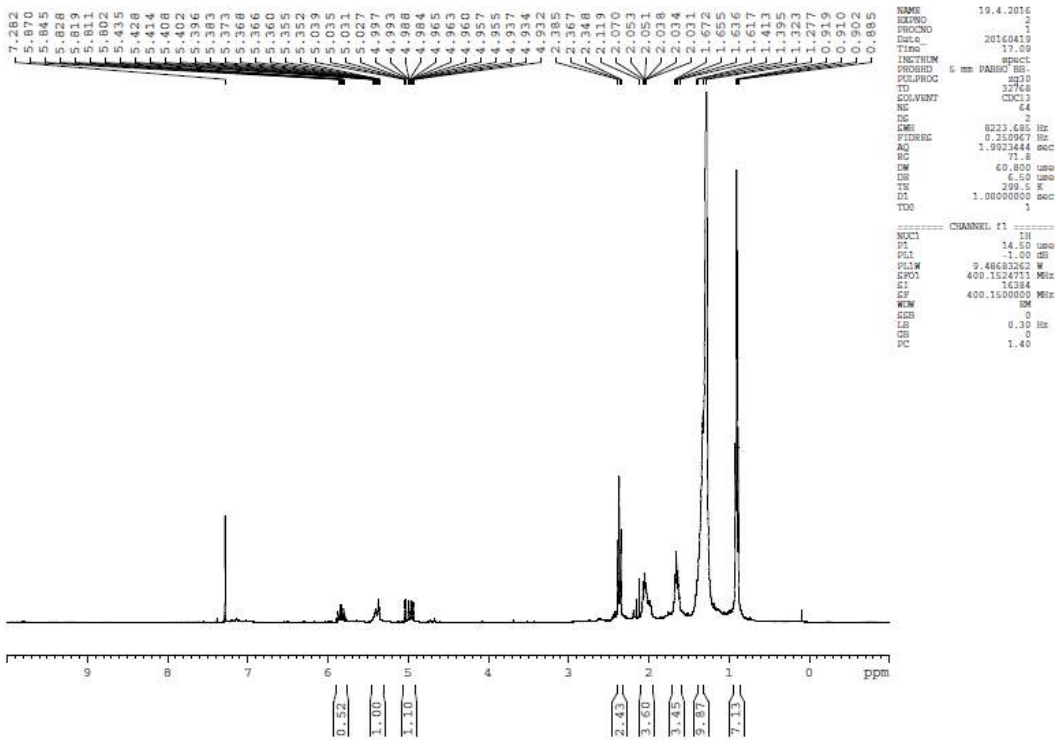

Figure 4.18 **The ^{1}H** NMR spectra of Rice Bran Wax pyrolytic oil

Table 4.18 NMR analysis of Rice Bran Wax pyrolytic oil

Hydrogen type	**Chemical shift (ppm)**	**Total hydrogen (%)**
Alkane C-H	0.8-1.4	58.42
Allylic, benzylic, adjacent to sp^2 carbon	1.5-2.4	32.58
Alkene =CH	4.9-6.0	9.01

.

The NMR of 1:3 pyrolytic oil showed the major presence of alkanes and aromatic and a very few amount of alkenes. The total percentage of hydrogen present in alkanes and aromatics present around 56% and 36%. Alkenes contribute to only 8.5%.

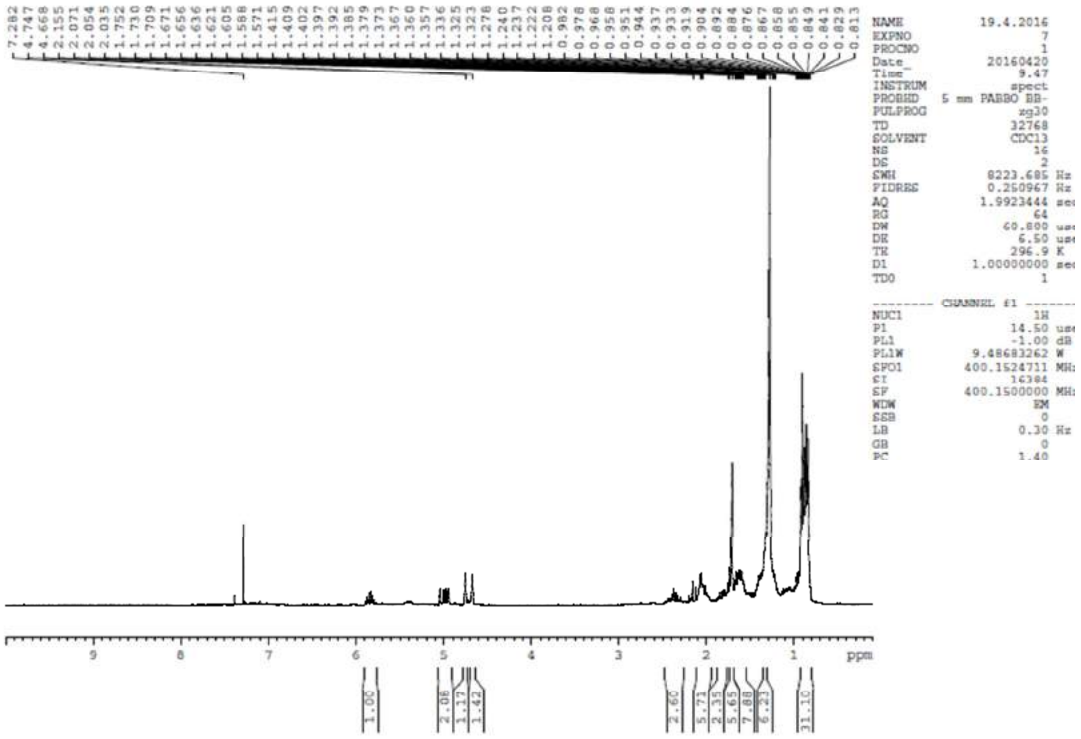

Figure 4.19 **The** ^{1}H NMR spectra of 1:3 ratio pyrolytic oil

Table 4.19 NMR analysis of 1:3 pyrolytic oil

Hydrogen type	**Chemical shift (ppm)**	**Total hydrogen (%)**
Alkane C-H	0.7-1.5	55.56
Allylic, benzylic, adjacent to sp^2 carbon	1.6-2.5	36.01
Alkene =CH	4.5-5.1	6.95
Alkene =CH	5.7-6.0	1.49

4.6 Characterization of the pyrolytic char

4.6.1 Proximate and ultimate analysis of char sample

The 1:3 ratio pyrolytic residues obtained at 550℃ was studied further for all presented analysis. The proximate and ultimate analysis of char has been summarized in Table 4.18. The proximate analysis which includes the determination of moisture, volatile matter, ash content and fixed carbon is primarily carried out to ascertain the quality of the residue

obtained after the pyrolysis and the ultimate analysis was used to determine the elemental composition regarding carbon, hydrogen, sulfur, nitrogen, and oxygen. Ultimate analysis showed that the carbon and oxygen content was more and fewer amounts of hydrogen, nitrogen and sulfur content was present. The higher carbon content shows that it can be used as a high-efficiency solid fuel in boilers. It can be used for the further gasification process to obtain hydrogen rich gas [10].

Table 4.20 Proximate and ultimate analysis of 1:3 char sample

Characteristics	**1:3 Char**
Proximate Analysis	
Moisture Content	1.57
Volatile Matter	10.8
Ash Content	47
Fixed Carbon	40.63
Ultimate Analysis	
C	46.60
H	1.36
N	0.04
S	0.83
O (By difference)	51.17
Empirical Formula	$C_1H_{0.35}N_{0.0007}S_{0.008}O_{0.81}$
C/H Molar ratio	2.85
C/O Molar ratio	1.21
Gross Calorific Value (MJ/Kg)	17.26

4.6.2 SEM Analysis

In this research, the SEM is used to investigate the surface morphology of the char. The char sample surface morphology with the different magnification (1000X, 2000X, 5000X) was investigated. The results showed that the char is highly porous, has the benefit of more adsorption sites for ions and provide space for nutrients and water medium [54]. The above statement confirms that it can be used as activated carbon.

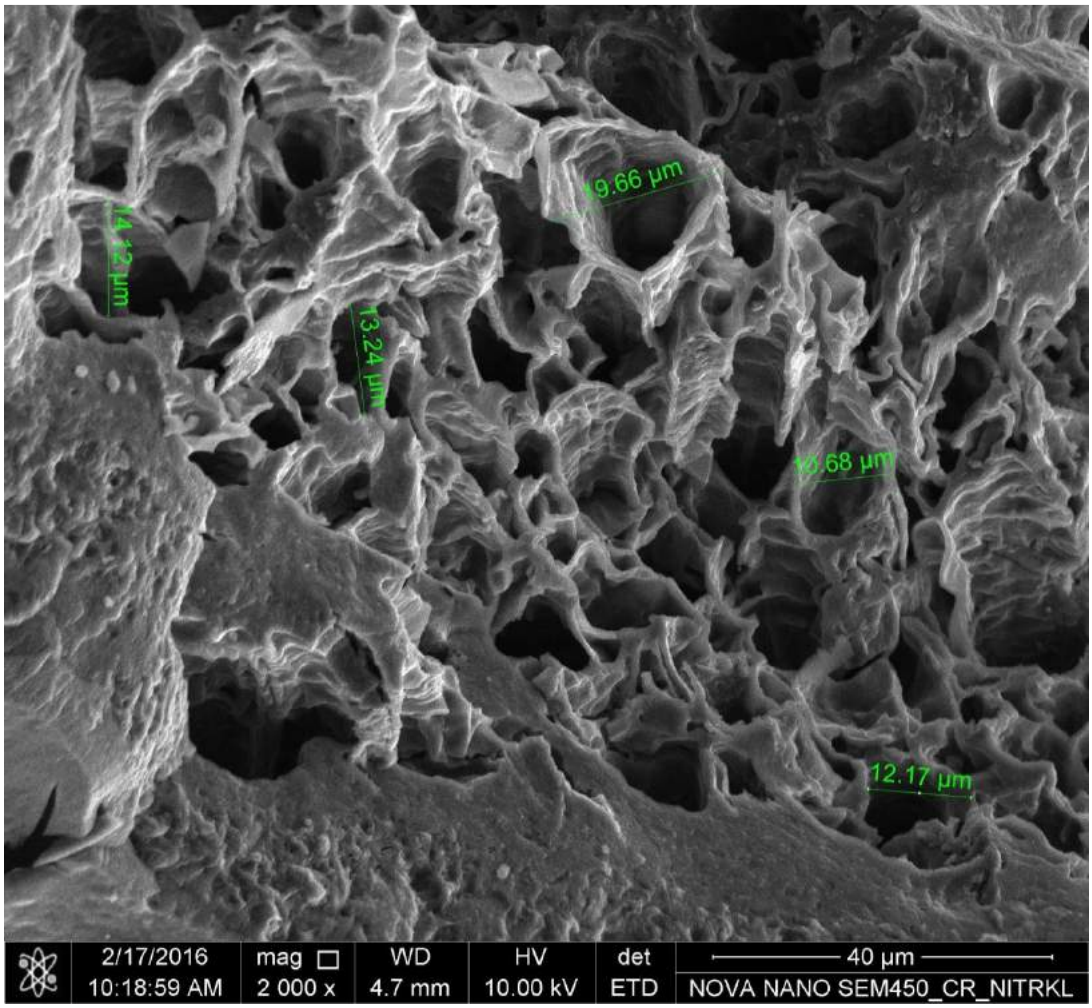

Figure 4.20 SEM of 1:3 char at 2000X

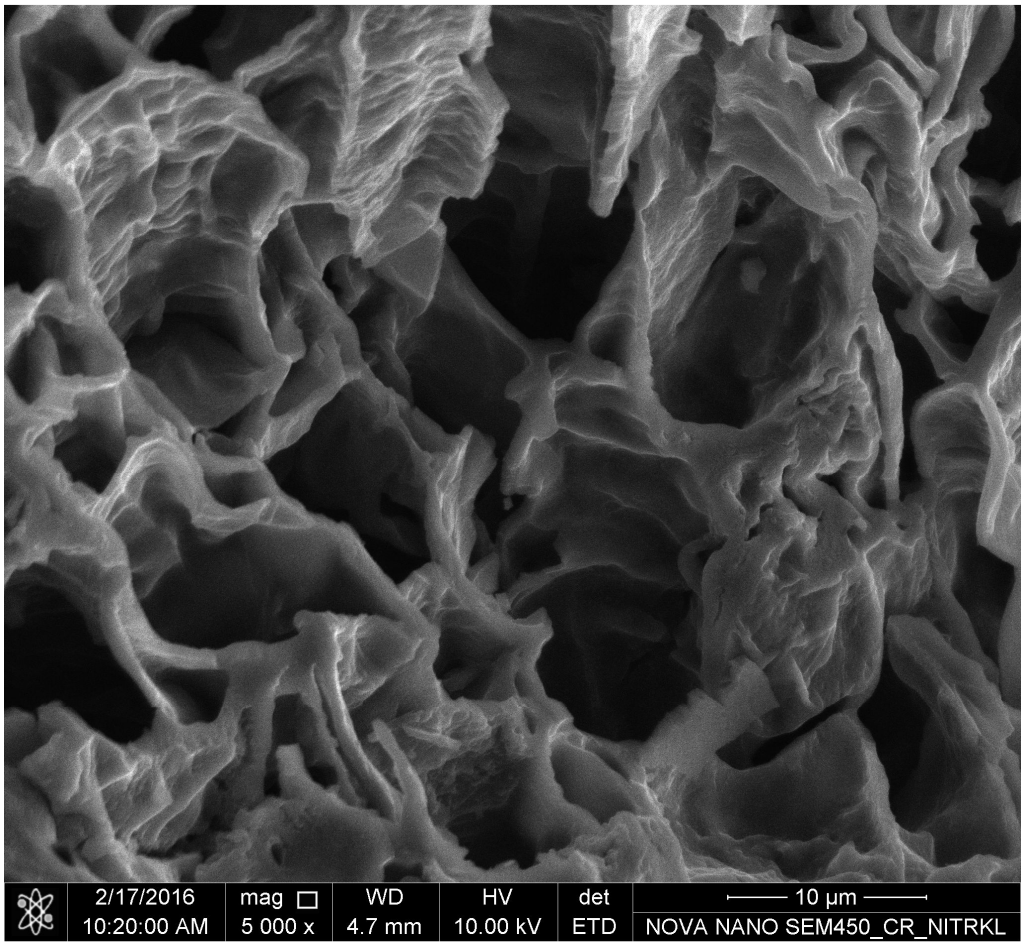

Figure 4.21 SEM of 1:3 char at 5000X

4.6.3 BET Analysis

From the Figure 4.19, the BET surface area was calculated by determining the slope and intercept of the graph between relative pressure and volume @ STP. By putting all the value in the BET equation, the surface area of the char sample was calculated as 12.621 m^2/gm.

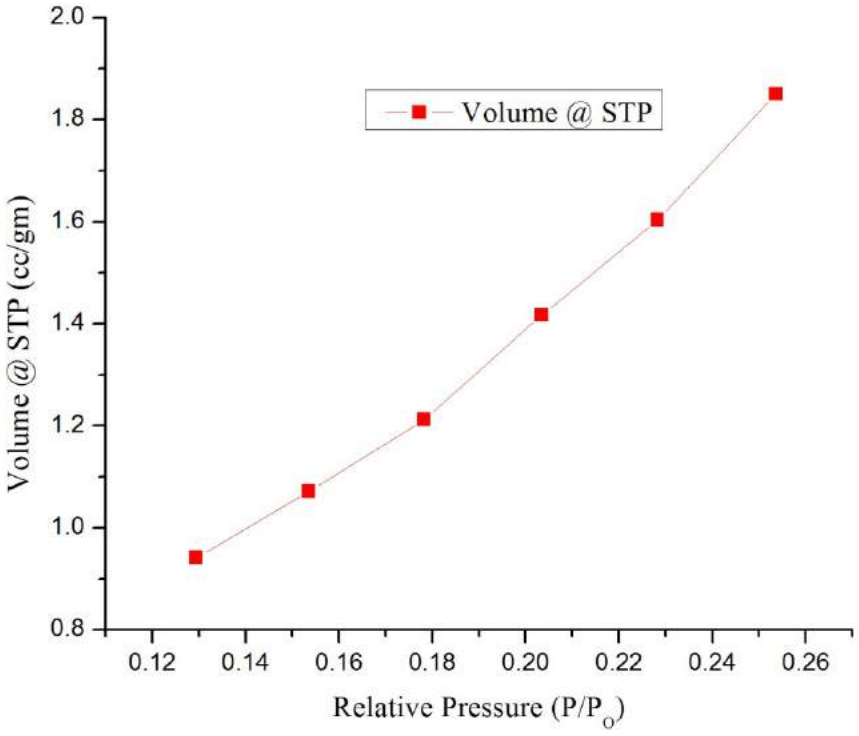

Figure 4.22 BET Graph of 1:3 char

Chapter5 Conclusions

5.1 Conclusion

Co-pyrolysis behavior of rice bran wax, waste polypropylene, and their blend were studied. By using this technique, a lot of benefits have been discovered like improving the quantity and quality of pyrolytic oil, improving waste management system, reducing the consumption of fossil fuels, and feasibility to economic analysis. The thermal co-pyrolysis has been carried out in a semi-batch reactor under different temperature ranges from 400°C to 650°C, and following conclusions were observed.

- On the basis of Thermogravimetric analysis, the decomposition pattern of PP, RBW and 1:1 ratio was found out to be in between 400℃ to 600℃. Furthermore, the results from TGA were compared with the experimental results.
- The best pyrolytic oil selected was 1:3 ratio. The optimum oil of 80.5 % was obtained at 550℃, having a calorific value of 43.76 MJ/Kg.
- It was also observed that with an increase in temperature both oil and gas was increased. This is due to the strong cracking of PP and RBW and at the same time, the secondary cracking takes place inside the reactor. But the char yield was decreased with increase in temperature. This shows the effect of temperature on production yield.
- It was also witnessed that as the amount of PP was increasing (e.g. 0:1, 1:1,2:1,3:1), the liquid yield was getting low, and as the quantity of RBW was increasing (e.g. 1:0, 1:2,1:3) the yield was getting high. This was due to the strong cracking of RBW as compared to PP.
- The obtained physical properties of the pyrolytic oil were fairly comparable to Diesel and Gasoline. The properties of the oil were a mixture of diesel and gasoline.
- From the chemical composition such as FTIR, GC-MS, and NMR spectroscopy, it was concluded that the functional groups present in the oil was mainly aliphatic and aromatic compounds, with the small composition of oxygenated compounds

such as ketones, aldehydes, acids, ethers, etc. From the GC-MS analysis around 70 compounds were detected of varying carbon chain length ranging between C_3 to C_{20}.

- The char of the oil was also investigated. From the BET and SEM analysis, it was concluded that the residue can be used as activated carbon and solid fuels for boilers.
- By considering all these results, it can be concluded that the oil obtained from co-pyrolysis of PP and RBW can be used as an alternative fuel after proper treatment.

5.2 Future Scope of the work

- To conduct catalytic pyrolysis of the different ratios of Rice Bran Wax and Polypropylene and to optimize the oil yield and enhance its physical and chemical properties.
- To develop a better experimental model which helps to improve the quality and quantity of the pyrolytic oil and the char.
- To study the engine performance test in I.C Engines.
- To collect the non-condensable gasses which were released into the environment and to investigate their composition.
- To study the kinetic behavior of Polypropylene and Rice Bran Wax using Thermogravimetric Analysis.

Chapter6 References

[1] "Overview of plastic: http://www.icpeenvis.nic.in/index2.aspx?slid=50&sublinkid=237&langid=1&mid=1.

[2] "Production of plastics worldwide from 1950 to 2014." http://www.statista.com/statistics/282732/global-production-of-plastics-since-1950/.

[3] F. Paradela, "Study of the co-pyrolysis of biomass and plastic wastes," *Clean Techn Env. Policy*, pp. 1–8, 2008.

[4] R. Miranda, H. Pakdel, C. Roy, and C. Vasile, "Vacuum pyrolysis of commingled plastics containing PVC II . Product analysis," *Polym. Degrad. Stab.*, vol. 73, pp. 47–67, 2001.

[5] A. K. Panda, "Studies on process optimization for production of liquid fuels from waste plastics," no. July 2011.

[6] J. Aguado, D. P. Serrano, and J. M. Escola, "Fuels from waste plastics by thermal and catalytic processes: A review," *Ind. Eng. Chem. Res.*, vol. 47, no. 21, pp. 7982–7992, 2008.

[7] "All-India Area, Production and Yield of Rice." http://www.airea.net/page/62/statistical-data/all-india-area-production-and-yield-of-rice.

[8] L. S. K. Dassanayake, D. R. Kodali, S. Ueno, and K. Sato, "Physical properties of rice bran wax in bulk and organogels," *JAOCS, J. Am. Oil Chem. Soc.*, vol. 86, no. 12, pp. 1163–1173, 2009.

[9] J. L. Easterly and M. Burnham, "Overview of biomass and waste fuel for power production," *Biomass*, vol. 10, no. 95, pp. 79–92, 1996.

[10] M. P. Pinthong, "Co-pyrolysis of Rice Husk, Polyethylene and Polypropylene Mixtures: A Kinetic Study," Kasetsart University, 2009.

[11] F. Abnisa, W. Mohd, and A. Wan, "A review on co-pyrolysis of biomass : An optional technique to obtain a high-grade pyrolysis oil," *Energy Convers. Manag.*, vol. 87, pp. 71–85, 2014.

[12] J. Chattopadhyay, C. Kim, R. Kim, and D. Pak, "Thermogravimetric characteristics and kinetic study of biomass co-pyrolysis with plastics," *Korean J.Chem. Engg*, vol. 25, no. 5, pp. 1047–1053, 2008.

[13] J. D. Martínez, A. Veses, A. M. Mastral, R. Murillo, M. V Navarro, N. Puy, A. Artigues, J. Bartrolí, and T. García, "Co-pyrolysis of biomass with waste tyres : Upgrading of liquid bio-fuel," *Fuel Process. Technol.*, vol. 119, pp. 263–271, 2014.

[14] L. Zhang, S. Xu, W. Zhao, and S. Liu, "Co-pyrolysis of biomass and coal in a free fall reactor," *Fuel*, vol. 86, pp. 353–359, 2007.

[15] "Overview of Natural Gas". http://naturalgas.org/overview/history/.

[16] "What are Plastics." http://www.icpeenvis.nic.in/index2.aspx?slid=48&sublinkid=235&langid=1&mid=1.

[17] A. Demirbas, "Pyrolysis of municipal plastic wastes for recovery of gasoline-range hydrocarbons," *J. Anal. Appl. Pyrolysis*, vol. 72, no. 1, pp. 97–102, 2004.

[18] T. C. Clive Maier, *Polypropylene: The Definitive User's Guide and Databook*. Elsevier Science, 2008.

[19] "Review on Development of Polypropylene Manufacturing," *R&D Report,*

Sumitomo Kagaku, vol. 2, pp. 1–11, 2009.
[20] S. Yuan, Z. Dai, Z. Zhou, X. Chen, G. Yu, and F. Wang, "Bioresource Technology Rapid co-pyrolysis of rice straw and a bituminous coal in a high-frequency furnace and gasification of the residual char," *Bioresour. Technol.*, vol. 109, pp. 188–197, 2012.
[21] A. K. Panda and R. K. Singh, "Experimental Optimization of Process for the Thermo-catalytic Degradation of Waste Polypropylene to Liquid Fuel," *Adv. Energy Eng.*, vol. 1, no. 3, pp. 1–11, 2013.
[22] A. Demirbaş, "Recovery of Chemicals and Gasoline-Range Fuels from Plastic Wastes via Pyrolysis," *Energy Sources*, vol. 27, no. 14, pp. 1313–1319, 2005.
[23] "World Energy Outlook 2000," *International Energy Agency*, p. 444, 2000.
[24] T. Bridgwater, "Biomass for energy," *J. Sci. Food Agric.*, vol. 1768, no. 2006, pp. 1755–1768, 2006.
[25] S. Czernik and A. V Bridgwater, "Overview of Applications of Biomass Fast Pyrolysis Oil," *Energy & Fuels*, no. 18, pp. 590–598, 2004.
[26] R. Muzyka, "Use of plastic waste as a fuel in the co-pyrolysis of biomass . Part I The effect of the addition of plastic waste on the process and products," *J. Anal. Appl. Pyrolysis*, vol. 107, pp. 265–275, 2014.
[27] J. A. Cunha, M. M. Pereira, and L. M. M. Valente, "Waste biomass to liquids : Low temperature conversion of sugarcane bagasse to bio-oil . The effect of combined hydrolysis treatments," *Biomass and Bioenergy*, vol. 35, pp. 2106–2116, 2011.
[28] L. Qiang, L. Wen-zhi, and Z. Xi-feng, "Overview of fuel properties of biomass fast pyrolysis oils," *Energy Convers. Manag.*, vol. 50, no. 5, pp. 1376–1383, 2009.
[29] Q. Cao, W. Bao, and Y. Lv, "Investigations into the characteristics of oils produced from co-pyrolysis of biomass and tire," *Fuel Process. Technol.*, vol. 90, pp. 337–342, 2009.
[30] R. Fahmi, "The effect of lignin and inorganic species in biomass on pyrolysis oil yields , quality and stability," *Fuel*, vol. 87, pp. 1230–1240, 2008.
[31] A. Oasmaa and S. Czernik, "Fuel Oil Quality of Biomass Pyrolysis Oils State of the Art for the End Users," *Energy & Fuels*, vol. 13, pp. 914–921, 1999.
[32] A. Oasmaa, J. Levander, and E. Tapola, "Physical characterisation of biomass-based pyrolysis liquids Application of standard fuel oil analyses," 1997.
[33] F. Abnisa, W. M. A. W. Daud, and J. N. Sahu, "Pyrolysis of Mixtures of Palm Shell and Polystyrene : An Optional Method to Produce a High-Grade of Pyrolysis Oil," *AIChE*, pp. 1–8, 2013.
[34] D. R. Mcilveen-wright, F. Pinto, L. Armesto, M. A. Caballero, M. P. Aznar, and A. Cabanillas, "A comparison of circulating fluidised bed combustion and gasification power plant technologies for processing mixtures of coal , biomass and plastic waste," *Fuel Process. Technol.*, vol. 87, pp. 793–801, 2006.
[35] V. I. Sharypo, N. G. Berego, and B. N. Kuznetso, "Co-pyrolysis of wood biomass and synthetic polymers mixtures . Part III : Characterisation of hea v y products," *J. Anal. Appl. Pyrolysis*, vol. 67, pp. 325–340, 2003.
[36] C. Shen, W. Chen, H. Hsu, J. Sheu, and T. Hsieh, "Co-gasification performance of coal and petroleum coke blends in a pilot-scale pressurized entrained-flow gasifier," *Int. J. Energy Res.*, vol. 26, no. February 2011, pp. 499–508, 2012.
[37] M. Brebu, S. Ucar, C. Vasile, and J. Yanik, "Co-pyrolysis of pine cone with synthetic polymers," *Fuel*, vol. 89, no. 8, pp. 1911–1918, 2010.
[38] N. S. Kasim, T.-H. Tsai, S. Gunawan, and Y.-H. Ju, "Biodiesel production from rice bran oil and supercritical methanol.," *Bioresour. Technol.*, vol. 100, no. 8, pp. 2399–2403, 2009.

[39] "Rice Bran Oil." http://www.riceactive.com/?page_id=203.
[40] A. P. Hasan, M. A. Wakil, and M. A. Kafy, "Prospect of rice bran for biodiesel production in Bangladesh," *Procedia Eng.*, vol. 90, pp. 746–752, 2014.
[41] S. Nandi, S. Ganguly, R. Bhattachryya, and C. Sumit Nandi, "Synthesis of Triacontanol Concentrate from Crude Rice Bran Wax by Microwave Treatment and Molecular Distillation," *Che Sci Rev Lett*, vol. 2, no. 5, pp. 387–392, 2014.
[42] A. R. Babu, "Recovery of liquid hydrocarbon fuels from waste plastics," NIT, Rourkela, 2007.
[43] G. M. Jeng, Y. Y. Yin, and J. B. Li, "Manufacture of Liquid Fuel by Catalytic Cracking Waste Plastics in a Fluidized Bed," *Energy Sources*, vol. 25, no. 6, pp. 577–590, 2003.
[44] A. K. Panda, R. K. Singh, and D. K. Mishra, "Thermolysis of waste plastics to liquid fuel: A suitable method for plastic waste management and manufacture of value added products—A world prospective," *Renew. Sustain. Energy Rev.*, vol. 14, no. 1, pp. 233–248, 2010.
[45] J. Scheirs and W. Kaminsky, "Feedstock Recycling and Pyrolysis of Waste Plastics: Converting Waste Plastics into Diesel and Other Fuels," *Feed. Recycl. Pyrolysis Waste Plast. Convert. Waste Plast. into Diesel Other Fuels*, pp. 1–785, 2006.
[46] H. Zhang, J. Nie, R. Xiao, B. Jin, C. Dong, and G. Xiao, "Catalytic co-pyrolysis of biomass and different plastics (polyethylene, polypropylene, and polystyrene) to improve hydrocarbon yield in a fluidized-bed reactor," *Energy and Fuels*, vol. 28, no. 3, pp. 1940–1947, 2014.
[47] D. Pradhan, "Analysis of Bio-Oil Produced by Co-Pyrolysis of Mahua Seed and Polystyrene," no. August 2015, pp. 1–6, 2016.
[48] F. Abnisa, W. M. A. W. Daud, S. Ramalingam, M. Naqiuddin, B. M. Azemi, and J. N. Sahu, "Co-pyrolysis of palm shell and polystyrene waste mixtures to synthesis liquid fuel," *Fuel*, vol. 108, pp. 311–318, 2013.
[49] V. I. Sharypov, N. Marin, and N. G. Beregovtsova, "Co-pyrolysis of wood biomass and synthetic polymer mixtures . Part I : influence of experimental conditions on the evolution of solids , liquids and gases," *J. Anal. Appl. Pyrolysis*, vol. 64, pp. 15–28, 2002.
[50] "Innovative Solutions for Thermal Analysis." http://instrument-specialists.com/.
[51] A. Olajire, C. Zhi, S. Hanson, and C. Wai, "Thermogravimetric analysis of the pyrolysis characteristics and kinetics of plastics and biomass blends," *Fuel Process. Technol.*, vol. 128, pp. 471–481, 2014.
[52] N. Kiran, E. Ekinci, and C. E. Snape, "Pyrolysis of virgin and waste polypropylene and its mixtures with waste polyethylene and polystyrene," *Waste Manag.*, vol. 24, pp. 173–181, 2004.
[53] S. Kumar, "Conversion of waste high-density polyethylene into liquid fuels," NIT Rourkela, 2011.
[54] T. Rout, D. Pradhan, R. K. Singh, and N. Kumari, "Journal of Environmental Chemical Engineering Exhaustive study of products obtained from coconut shell pyrolysis," *Biochem. Pharmacol.*, no. 2015, 2016.

Appendix

GC-MS of Polypropylene oil

Compound Name	Area %	Formula
Aliphatic Compounds		
Cyclobutane	1.92	C_4H_8
Octane	2.64	C_8H_{18}
2-Butene	0.63	C_4H_8
1-Tetradecene	2.9	$C_{14}H_{28}$
1-cis,2-cis,3-trans-trimethylcyclopentane	1.37	C_8H_{16}
Cyclopentane, 1, 2, 3-trimethyl-, (1.alpha. 2. alpha., 3.alpha.)-	1.37	C_8H_{16}
1-Azabicyclo[2.2.2]octane	3.94	$C_7H_{13}N$
Decane	0.53	$C_{10}H_{22}$
Heptane	3.45	C_7H_{16}
3-Amino-1-azabicyclo[2.2.2]octane	0.92	$C_7H_{14}N_2$
8-Propyl-1,5-Diazabicyclo[3.2.1]-Octane	1.92	$C_9H_{18}N_2$
n-Octane	1.73	C_8H_{18}
2,4-Diazapentane	1.19	$C_3H_{10}N_2$
2-Hexene	1.10	C_6H_{12}
5,7,7-Trimethyl-6,8-dioxabicyclo[3.2.1]octane	0.98	$C_9H_{16}O_2$
2-Heptene	0.59	C_7H_{14}
Undecane, 6,6-Dideutero-2-Methyl-	0.85	$C_{12}H_{22}O_2$
Amines & Amides		
2-Propyn-1-amine	0.39	C_3H_5N
Methylamine, N-(1-ethylpentylidene)- (CAS)	1.83	$C_8H_{17}N$
Ethanimidamide	0.63	$C_2H_6N_2$
N,1,3-trimethylcyclopentylamine	1.20	$C_8H_{17}N$
1,3-Butanediamine, N,N,N',N'-tetramethyl-	0.59	$C_8H_{20}N_2$
2-Propen-1-amine	3.07	C_3H_7N
Cyclopentanamine	2.90	$C_5H_{11}N$
N-Isopropyl-2-azido-2-ethylbutanimine	2.88	$C_9H_{19}N_4$
3,3,5-Trimethylcyclohexylamine	1.69	$C_9H_{19}N$
4-Piperidinecarboxylic acid hydrazide	1.35	$C_6H_{13}N_3O$
Ketones		
1-(1H-Imidazol-2-yl)-ethanone	1.02	$C_5H_6N_2O$
Spiro[2.4]heptan-4-one	0.69	$C_7H_{10}O$
Bicyclo[3.3.1]nonan-2-one	4.31	$C_9H_{14}O$
3-(2-hydroxyethyl)-2,3-dimethylcyclopentanone	10.13	$C_9H_{16}O_2$
3-(N-Ethyl)imino-4-heptanone	0.87	$C_{19}H_{17}NO$
8-Azabicyclo[3.2.1]octan-1-one	2.29	$C_7H_{12}NO$
3-Piperidinone	3.16	C_5H_9NO
5-Methylcycloheptane-1,4-dione	0.79	$C_8H_{12}O_2$
Aldehydes		

E-2-decenal	1.87	$C_8H_{13}O$
2-Nonenal	0.51	$C_9H_{16}O$
2-Propenal, 3-(dimethylamino)-3-[(1-methylethyl)amino]-	3.23	$C_8H_{16}N_2O$
Alcohols & Phenols		
1,2-Dimethylcyclohexan-1-ol	9.55	$C_8H_{16}O$
4-(Pyrrolidinyl)but-2-en-4-ol	1.23	$C_8H_{15}O$
Acids & Esters		
Formic Acid	3.94	CH_2O_2
Other Heterocyclic Compounds		
2-[3-[N-Aziridyl]propyl]aminomethyltetrahydropyran	1.77	$C_9H_{21}IrN_3O$
alpha.-[2-[N-Aziridyl]ethylamino]isobutyronitrile	1.33	$C_6H_{14}IrN_4$
1,2,4-Oxadiazole, 3-(5-amino-1,3,4-oxadiazol-2-yl)-5-diethylaminomethyl-	1.46	$C_9H_{14}N_6O_2$

GC-MS of Rice Bran Wax oil

Compound Name	Area %	Formula
Aliphatic & Aromatic Compounds		
Heptane	1.55	C_7H_{16}
5-hydroxy-5-dideutero-1,2-pentadiene	4.05	$C_5H_6D_2O$
2-Ethyl-2-azabicyclo[2.1.1]hexane	0.72	$C_7H_{13}N$
Cyclopropane	0.76	C_3H_6
5-hydroxy-5-dideutero-1,2-pentadiene	4.70	$C_5H_6D_2O$
Octane	2.33	C_8H_{16}
3-Trifluoroacetoxydodecane	0.40	$C_{14}H_{25}F_3O_2$
2,4-Diazapentane	0.60	$C_3H_{10}N_2$
2-Hexene	3.84	C_6H_{12}
1,1,2-Trimethyl-1-silacyclobutane	4.78	$C_6H_{14}Si$
2-deutero-1,4-dimethylbenzene	0.72	C_8H_9D
Amines & Amides		
N-Acetyl-3-pentenyl-1-amine	4.83	$C_7H_{13}NO$
Piperidine,	2.69	$C_5H_{11}N$
N-[3-Methylaminopropyl]aziridine	0.60	$C_6H_{14}N_2$
Aziridine	0.58	C_2H_5N
1-Butanamine	1.80	$C_4H_{11}N$
3,3-Dimethylcyclohexylamine	3.69	$C_8H_{17}N$
Methanimine,C-ethoxycarbonyl,N-ethoxycarbonylmethyl	3.43	$C_8H_{13}NO_4$
Methanamine, N-[2-methyl-1-(1-methylethyl)butylidene]-	6.40	$C_9H_{19}N$
1H-Azepine	4.24	C_6H_7N
3,3-Dimethylcyclohexylamine	1.89	$C_8H_{17}N$
Ketones		

Bicyclo[3.3.1]nonan-2-one	5.36	$C_9H_{14}O$
3-(N-Ethyl)imino-4-heptanone	15.33	$C_9H_{17}NO$
2H-Azepin-2-one	2.03	C_6H_5NO
5-Methylcycloheptane-1,4-dione	1.67	$C_8H_{12}O_2$
1-Chloro-3-bromo-1,3-dioximino-2-propanone	7.92	$C_3H_2BrClN_2O_3$
1,3-diphenyl-4-(2-(2-hydroxybenzylidene)aminobenzyl)-2-pyrazolin-5-one	3.84	$C_{29}H_{23}N_3O_2$
Aldehydes		
6,7-Dideuteriododec-6-enal	1.55	$C_{12}H_{20}D_2O$
Undecanal	1.04	$C_{11}H_{22}O$
Hexanal (CAS)	6.99	$C_6H_{12}O$
2,2,3,3,4,4 hexadeutero octadecanal	2.20	$C_{18}H_{30}D_6O$
2-Decenal	0.58	$C_{10}H_{18}O$
Alcohols & Phenols		
Ribitol	2.73	$C_6H_{12}O_5$
1-Dodecanol (CAS)	0.49	$C_{12}H_{26}O$
Phenol	11.45	C_6H_6O
3,6-Diazaoctane-1,8-diol	11.45	$C_6H_{16}N_2O_2$
Acids & Esters		
Methyl ester of hexanesulfonic acid	1.04	$C_7H_{16}O_3S$
3-deuterio-2-(1-methylethenyl)-2-pentenoic acid	2.20	$C_8H_{11}DO_2$
Sulfurous acid, octyl 2-pentyl ester	0.48	$C_{13}H_{28}O_3S$
1-propen-2-ol, acetate	1.35	$C_5H_8O_2$
Other Heterocyclic Compounds		
1,2,4-Oxadiazole, 3-(5-amino-1,3,4-oxadiazol-2-yl)-5-diethylaminomethyl-	4.22	$C_9H_{14}N_6O_2$
3.beta.,7.beta.-Dihydroxycholestane-5.alpha.,7.alpha.-carbolactam	3.84	$C_{28}H_{46}O_4$

GC-MS of 1:3 Oil

Compound Name	**Area %**	**Formula**
Aliphatic & Aromatic Compounds		
1,4-Dioxocyclohexane	0.69	$C_6H_8O_2$
Cyclobutane	0.69	C_4H_8
2-deutero-1,4-dimethylbenzene	0.88	C_8H_9D
1,1,1,2-tetrafluoro-2-tridecene	1.37	$C_{13}H_{22}F_4$
2-Trifluoroacetoxytetradecane	1.37	$C_{16}H_{29}F_3O_2$
3,4-Dimethylheptane	1.37	C_9H_{20}
Azacyclohexane	0.42	$C_5H_{11}N$
5-hydroxy-5-dideutero-1,2-pentadiene	4.19	$C_5H_6D_2O$
Octane, 4-methyl-	2.07	C_9H_{20}
2,4-Diazapentane	1.63	$C_3H_{10}N_2$

cis-3-Methyl-2-Hexene	9.21	C_7H_{14}
1,1,2-Trimethyl-1-silacyclobutane	1.83	$C_6H_{14}Si$
Amines & Amides		
2,2-Dimethylaziridine	2.34	C_4H_9N
1-trideutero acetyl-2-methylaziridine	1.08	$C_5H_8D_3NO$
Aziridine, 2,2-dimethyl-	2.07	C_4H_9N
2,2-Dimethylethylenimine	1.85	C_4H_9N
Piperidine (CAS)	2.07	$C_5H_{11}N$
N-[3-Hexylaminopropyl]aziridine	1.42	$C_{11}H_{24}N_2$
3,4,4-trimethyl-1,2,6-oxadiazine N-oxide	0.66	$C_6H_{10}N_2O_2$
2,5-Diisopropylpiperazine	0.66	$C_{10}H_{22}N_2$
N-Acetyl-3-pentenyl-1-amine	4.68	$C_7H_{13}NO$
N,N-Diethyl-1-methyl-1,3-propanediamine	0.69	$C_8H_{20}N_2$
N-[3-Methylaminopropyl]aziridine	0.79	$C_6H_{14}N_2$
n-Octyl methyl imine	1.68	$C_9H_{19}N$
2,2-Dimethyl-1-isopropylazetidine	1.74	$C_8H_{17}N$
Acetoacetamide, N,N-diethyl-	0.96	$C_8H_{15}NO_2$
N-Methylhomopiperazine	1.04	$C_6H_{14}N_2$
Piperidine, 2,3-dimethyl-	5.79	$C_7H_{15}N$
Methanimine,C-ethoxycarbonyl,N-ethoxycarbonylmethyl	1.83	$C_8H_{13}NO_4$
N-[3-Methylaminopropyl]aziridine	1.88	$C_6H_{14}N_2$
3-Chloro-6-[3-dimethylaminopropylamino]pyridazine	1.88	$C_9H_{15}ClN_4$
2,2,3,3-Tetramethylazetidine	2.09	$C_7H_{15}N$
Ketones		
Bicyclo[3.3.1]nonan-2-one	6.51	$C_9H_{14}O$
Valeric acid, 3,5-dihydroxy-2,4-dimethyl-, .delta.-lactone	2.07	$C_7H_{12}O_3$
3-(N-Ethyl)imino-4-heptanone	12.25	$C_9H_{17}N$
8-Azabicyclo[3.2.1]octan-1-one	0.69	$C_7H_{12}NO$
5-Methylcycloheptane-1,4-dione	3.69	$C_8H_{12}O_2$
1-Chloro-3-bromo-1,3-dioximino-2-propanone	16.2	$C_3H_2BrClN_2O_3$
2-Hexylcyclobutanone	3.01	$C_{10}H_{18}O$
3-Ethenyl-3-hydroxy-4-methylcyclohexanone	1.95	$C_9H_{14}O_2$
Aldehydes		
Hexanal (CAS)	5.77	$C_6H_{12}O$
Alcohols & Phenols		
2,6-Dimethylcyclohexanol	3.57	$C_8H_{16}O$
1,5-Dimethyl-2-(2-propyl)cyclopentanol	1.16	$C_{10}H_{20}O$
1-Tridecanol	5.04	$C_{13}H_{28}O$
Acids & Esters		
Methylcyclohexylacetate	7.56	$C_9H_{16}O_2$
Butylcyanate	1.74	C_5H_9NO
Pentanoic acid, propyl ester (CAS)	7.56	$C_8H_{16}O_2$
Tetrahydrogeranyl acetate	3.01	$C_{12}H_{20}O_2$

Nonyl chloridocarbonate	1.83	$C_{10}H_{19}ClO_2$
ethyl 2-benzoyl-3-phenylamino-2-propenoate	3.21	$C_{18}H_{17}NO_3$
12-Oxotridecanoic acid	2.09	$C_{13}H_{24}O_3$
Other Heterocyclic Compounds		
2-Methyl-1-cyclopenten-1-carbonitrile	0.88	C_7H_9N
Urea, triethyl- (CAS)	0.59	$C_7H_{16}N_2O$
3,4,4-trimethyl-1,2,6-oxadiazine N-oxide	0.66	$C_6H_{10}N_2O_2$
2-Methoxytetrahydropyran	2.15	$C_6H_{12}O_2$
alpha.-[2-[N-Aziridyl]ethylamino]isobutyronitrile	0.63	$C_6H_{14}IrN_4$
4-Chloro-3,5-dimethylisoxazole	7.56	C_5H_6ClNO

Dissemination

Journal Articles

1. The manuscript has been communicated to "Bioresource technology- journal- Elsevier publication."